
THE JOURNAL

OF THE

Society of Dyers and Colourists

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THE SOCIETY OF DYERS AND COLOURISTS

The Society of Dyers and Colourists was founded in Bradford in 1884, with the object of "promoting Scientific and Technical Knowledge among Textile Colourists, and the general advancement of the interests of the tinctorial and allied industries excluding all questions connected with wages and trade regulations."

The Society now has eight Sections—Huddersfield, London, Manchester, Midlands, Northern Ireland, Scottish, West of England and South Wales, and West Riding—with four Junior Branches—Bradford, Leeds, Manchester, and Scottish. It has two affiliated societies—The Society of Dyers and Colourists of Australia and the Dyers and Colourists Association of South Africa.

Objects

To promote the advancement of science and technology, especially in the theory and practice of the tinctorial arts.

To provide means for the wider dissemination and interchange of knowledge concerning the science and technology of colour and colouring matters, of their methods of application, and of the materials to which they may be applied.

To encourage education and research in any or all of the above subjects.

And for the furtherance of these objects—

To hold meetings for the reading of papers, for lectures, and for discussions.

To publish a *Journal*.

And to do all such other things as may be conducive to the attainment of these objects.

Election of Officers and Members of Council

Officers and Members of Council—other than the President and President-elect, who are nominated by Council and elected at the Annual General Meeting—are elected by a Postal Ballot of the members.

The attention of members is drawn to Bye-laws No. 12–21 inclusive and 22–26 inclusive, which relate to Officers and Members of Council respectively.

Nominations must be received by the Honorary Secretary of the Society six weeks prior to the date of the Annual General Meeting.

Members and Junior Members

Persons desirous of joining the Society as Ordinary Members or Junior Members may obtain Application Forms from the General Secretary or from the Honorary Secretary of any Section of the Society. Applications must be proposed and seconded by members to whom the applicants are known personally. The rates of annual subscription are as follows—

- (i) Ordinary Members—£3 3s. 0d.
- (ii) Junior Members (under 21 years of age)—15s. 0d.
- (iii) Ordinary Members between the ages of 21 and 25 years who are students, i.e. who are pursuing an accepted course, full or part time, at a recognised technical college or university and vouched for by the head of their department or other responsible person—15s. 0d.
- (iv) Other Ordinary Members between the ages of 21 and 25 years—£2 2s. 0d.
- (v) Members having had continuous membership of the Society for forty years to be given the option of paying half the current annual subscription for Ordinary Members.
- (vi) Members having had continuous membership of the Society for fifty years—the annual subscription to be waived entirely.
- (vii) During the period of national service the annual subscription may be waived. Such members will be given the opportunity of continuing to receive the *Journal* without charge.

Members residing abroad are particularly requested to inform the General Secretary by separate post when forwarding their subscriptions.

* Published February 1960

Diplomas in Tinctorial Technology

The Society confers diplomas in tinctorial technology on suitably qualified members. These distinctions are in two grades—the Associateship (A.S.D.C.) and the Fellowship (F.S.D.C.). To obtain the Associateship candidates are required to pass the prescribed examinations and to furnish evidence of satisfactory general education and of training and experience in at least one branch of the manufacture or application of colouring matters. The Associateship has been accepted as a degree equivalent for the purposes of the Burnham Main and Technical Reports. The Fellowship is conferred on senior members who have attained high standing in the knowledge and practice of tinctorial technology. Students who intend to take the Society's examination are strongly recommended to become Registered Students, so that their studies and preparation may be directed effectively.

Copies of the regulations and syllabuses may be obtained on application to the offices of the Society.

The Journal

All members of the Society receive a copy of the *Journal* monthly.

Subscribers may receive the *Journal* for twelve months on payment of £5 5s. 0d.

Back numbers are supplied at 8s. 9d. per copy.

Communications on any subject related to the objects of the Society, especially such as are of an original character, are invited for consideration for publication in the *Journal*. Such Communications in the first instance should be addressed to the Editor at the offices of the Society.

General communications, including enquiries or orders for advertisements, should be addressed to the General Secretary.

Reprints of Lectures and Communications

Reprints of all lectures and communications are available if ordered immediately after publication. The charges (postage included) are as follows—Single copies 3s. 4d. each; per dozen copies up to and including 8 pages 16s. 0d., and for papers occupying more than 8 pages of the *Journal* 22s. 6d.

Abstracts Section

One-sided copies of the Abstracts, suitable for pasting on cards, are available at a charge of £2 0s. 0d. per annum.

Free Advertisements

For the convenience of members a limited number of advertisements relating to SITUATIONS WANTED may be inserted in the *Journal* gratis. Such advertisements must not exceed 24 words in length.

Replies may be addressed *Box—, Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire.*

Notice to Authors of Papers

The MSS. of all papers communicated to or read before the Society become the property of the Society. They should be addressed to the Editor at the offices of the Society and should arrive, if possible, before the monthly meeting of the Publications Committee, which is normally held on the third Tuesday in each month. Authors must not allow their papers to be published elsewhere before they have appeared in the Society's *Journal*. Should prior publication take place without the sanction of the Publications Committee, the paper will be printed only as an abstract or summary.

Manuscripts submitted for publication in the *Journal* should be typewritten (double spacing) on good quality paper, using one side of the paper only and leaving a margin at least 1 in. wide on the left-hand side. The time taken in refereeing papers (both lectures and communications) will be reduced to a minimum when authors submit two copies of the typescript.

In view of the high costs of publication, it is essential that authors should be as concise as possible. When experimental procedure has already been published, a literature reference to the paper containing the details is sufficient, and well known experimental methods should be described only very briefly.

Introductory paragraphs describing the aims of the investigation and the method of attack are desirable, and should be followed by the experimental results and their discussion. There should be a brief summary for insertion at the beginning of the paper. Centre headings should be employed sparingly. Side headings should be indented and underlined, and run into the text to which they apply by means of a dash. References to the literature should be numbered consecutively, using superscript numbers without brackets immediately following the text words or author's name to which they refer.

The list of references should be given at the end of the manuscript, and the abbreviations used should be, as far as possible, those given in the "List of Periodicals Abstracted" included at the end of the Index to the preceding year's *Journal*. Reference numbers in this list should be neither enclosed in brackets nor followed by full-stops. As far as possible throughout the manuscript the abbreviations listed in the Annual Index should be used. Tables should be numbered consecutively in Roman numerals and Figures in Arabic numerals.

The number of figures and graphs should be kept as low as possible, and results should be presented in the form of either tables or graphs, not both. Drawings should be carefully prepared, preferably in Indian ink, on plain white drawing paper, tracing paper or cloth, or, preferably, Bristol board (but duplicate drawings for refereeing purposes need be only roughly prepared). Graphs should be enclosed in a complete frame; co-ordinate lines should be omitted, except for very short lengths along the axes. Experimental points should be indicated by symbols selected from the following fourteen, which are readily available to the printer—

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In a series of Figures containing graphs of similar type, consistent use of symbols will be a help to the reader. In preparing drawings the author must see that thickness of and separation between lines and size of experimental points are adequate for reduction of the drawings, usually to column width (about 2½ in.). Any numbering or lettering on the drawings should be indicated lightly in pencil, *not* drawn in ink.

Twenty-five free copies of a reprint are supplied to the author of an original paper published in the *Journal*, or fifty free copies are supplied when there are two or more authors, and a further number may be purchased from the Society at the rates given above.

Copyright

Original articles, papers, and communications printed in this *Journal* are copyright. Subject to full acknowledgment being made, up to, but not exceeding, 800 words may be published elsewhere, but application for permission to reprint *in extenso* should be addressed to the Editor of the *Journal* at the offices of the Society.

The Society subscribes to the Royal Society Fair Copying Declaration (J.S.D.C., 66, 54 (Jan. 1950); 67, 236 (June 1951)).

The Society's Library

Many of the books and periodicals reviewed or abstracted in the *Journal* since 1948 (and in some cases earlier) are retained by the Society, and may be borrowed by members. Enquiries and applications should be directed to the Editor at the offices of the Society.

Historical Records

The Society is glad to receive gifts of old books, pattern cards, and other documents for inclusion if suitable in its collection of historical records related to the tinctorial arts.

Library of the Chemical Society—Loan of Books

Members of the Society may borrow books from the very extensive collection of works on pure and applied chemistry in the Library of the Chemical Society, by applying direct to *The Librarian, The Chemical Society, Burlington House, Piccadilly, London W. 1* (REGent 0675-6), and referring to their membership of the Society of Dyers and Colourists.

Deposit of Sealed Communications

The Society is prepared to receive from members and others and to keep as deposits Sealed Communications dealing with any subject relating to the theory or practice of the dyeing, printing, and kindred industries.

Further particulars will be supplied on application.

MEDALS AND AWARDS

Honorary Members of the Society

1886	Sir H. E. ROSCOE, M.P.	1934	H. GRANDAGE
1902	Dr. F. H. BOWMAN	1934	CHRISTOPHER RAWSON
1908	Prof. C. GRAEBE	1941	Prof. E. C. C. BALY, C.B.E.
1908	Prof. C. LIEBERMANN	1944	Prof. F. M. ROWE
1911	Prof. ADOLF VON BAEYER	1946	JAMES S. RIDSDALE
1914	Count HILAIRE DE CHARDONNET	1947	Dr. C. J. T. CRONSHAW
1917	Prof. ARTHUR G. GREEN	1948	H. JENNISON, M.C.
1919	R. VIDAL	1950	GEORGE E. HOLDEN, C.B.E.
1920	The Prime Warden of the Worshipful Company of Dyers (<i>ex officio</i>)	1953	JOHN BARRITT, O.B.E.
1921	HORACE A. LOWE	1954	FRED SCHOLEFIELD
1923	CHARLES F. CROSS	1954	Dr. C. M. WHITTAKER
1925	MAURICE PRUD'HOMME	1955	Sir ROBERT ROBINSON, O.M., Nobel Laureate
1927	ERNEST HICKSON	1956	FRED SMITH
1928	Dr. R. E. SCHMIDT	1959	H. H. BOWEN
1931	Dr. ALFRED RÉE	1959	W. H. CADY
1932	Prof. W. M. GARDNER	1959	CLIFFORD PAINE
1934	GEORGE DOUGLAS		

The following have been *ex officio* Honorary Members of the Society, the later dates indicating termination or change in the title of the office—

1886-1920	The Worshipful Master of the Dyers' Company	1900-1905	W. E. B. PRIESTLEY, Chairman of the Technical Instruction Committee of the Bradford City Council
1886-1900	The President, Bradford Technical College		



The Perkin Medal

The Perkin Medal is an excellent representation of the head of Sir William Perkin, the founder of the coal-tar colour industry, and President of the Society in 1907.

This medal is awarded for discoveries or work of outstanding importance in connection with the tinctorial arts.

List of Recipients

1908	Professors GRAEBE and LIEBERMANN	Synthesis of Alizarin
1911	Prof. ADOLF VON BAEYER	Synthesis of Indigo
1914	Comte HILAIRE DE CHARDONNET	Artificial Silk
1917	Prof. A. G. GREEN	Primuline
1919	R. VIDAL	Sulphur Black
1921	HORACE LOWE	Permanent Lustre on Cotton
1923	C. F. CROSS	Discovery of Viscose
1925	M. PRUD'HOMME	Aniline Black and Alizarin Blue
1928	Dr. R. E. SCHMIDT	For Epoch-making Discoveries of Anthraquinone Derivatives and Dyestuffs therefrom
1938	Dr. H. DREYFUS	For Discoveries and Work of Outstanding Importance in Connection with the Development of the Cellulose Acetate Rayon Industry in England
1938	J. BADDILEY	In recognition of his National Services for the Renaissance of the British Dyestuffs Industry through Many Important Investigations in the Field of Colour Chemistry Conducted or Directed by him
1950	Prof. J. B. SPEAKMAN	In recognition of his Outstanding Contributions to the Science and Technology of Textiles
1954	Dr. A. ZITSCHER	For his Work leading to the Discovery of the New Class of Azoic Dyes, based on the Arylamides of <i>o</i> -Hydroxy-carboxylic Acids
1956	Dr. W. H. CAROTHERS (posthumous award)	For the Discovery of Nylon
	JOHN R. WHINFIELD, C.B.E.	For the Discovery of Terylene

The Perkin Medal—continued

1959 Dr. C. J. T. CRONSHAW

As a Leader under whose Enthusiastic Guidance the Phthalocyanine Pigments and derived Textile Dyes were first made available and their Basic Constitution established

J. T. MARSH

For Outstanding Contributions to the Practice and the Literature of Textile Chemistry

**The Medal of
the Society of Dyers and Colourists**

This Medal was instituted by the Society in 1908. The design indicates that the work of the dyer (centre figure) is both a science (right background) and an art (left foreground).

1908–1927 The Medal was occasionally awarded as a recognition of work of exceptional merit carried out under the Society's Research Scheme.

From 1928 The Medal was awarded as a recognition of exceptional services (a) to the Society or (b) in the interests of the Tintorial and Allied Industries.

List of Recipients**Gold Medal**

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|------|-------------------------|---|
| 1928 | ERNEST HICKSON | Exceptional Services rendered to the Society as Chairman of the Publications Committee 1897–1925, and Chairman of <i>Colour Index</i> Committee |
| 1930 | ARTHUR SILVERWOOD | Exceptional Services rendered to the Society as Honorary Secretary 1913–1930 |
| 1933 | Prof. WALTER M. GARDNER | Distinguished Services as Editor of the Society's <i>Journal</i> 1900 to 1932 |
| 1934 | Prof. F. M. ROWE | Exceptional Services to the Society and to the Tintorial Industries as Editor of the <i>Colour Index</i> 1924 and the Supplement 1928 |
| 1940 | F. L. GOODALL | Valuable Services to the Tintorial Industries by his work on the Theory and Practice of Wool Dyeing |
| 1943 | C. M. WHITTAKER | In recognition of Exceptional Services in promoting Scientific and Technical Knowledge amongst Textile Colourists, and for Sustained and Outstanding Service to the Society |
| 1946 | H. H. BOWEN | For Outstanding Services to the Society and in recognition of his Chairmanship of the Publications Committee for a period of twenty years |
| | H. H. HODGSON | For Outstanding Services to the Society and for his series of Sustained Experimental and Theoretical Contributions to those chapters of Organic Chemistry which are the essential scientific background to the Dyestuffs Industry |
| 1947 | FRED SMITH | For Exceptional Services to the Society over a period of thirty-seven years comprising Chairman, West Riding Section; Member of Council and of many important Committees |
| | F. SCHOLEFIELD | In recognition of Exceptional Services to the Society in the advancement of Tintorial Technology both in theory and practice |
| 1948 | G. G. HOPKINSON | For Valuable Services rendered to the Society and to the Dyeing Industry |
| 1949 | S. M. NEALE | For his Pioneer Work in the Application of the Methods of Physical Chemistry to the Elucidation of the Phenomena of Dyeing, more particularly of Cellulosic Materials with Substantive Dyes |
| 1950 | P. W. CUNLIFFE | For Outstanding Services to the Society and to the Tintorial and Allied Industries |
| | H. FOSTER | For Outstanding Services to the Society |

Gold Medal—continued

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| 1951 | W. KILBY | For Work on the Development of a Molten Metal Process of Continuous Dyeing |
| 1953 | H. A. TURNER | For his Valuable Researches contributed to the Tinctorial Industries |
| 1954 | G. S. J. WHITE | For Exceptional Services to the Society and to the Tinctorial and Allied Industries |
| 1955 | P. W. CUNLIFFE (Bar) | For Continued Valuable Services to the Society as Chairman of the Fastness Tests Co-ordinating Committee |
| 1956 | C. O. CLARK | For Outstanding Services to the Society |
| 1957 | J. BARRITT, O.B.E. | For Exceptional Services to the Society as Chairman of the <i>Colour Index</i> Editorial Panel |
| 1958 | H. BLACKSHAW | For Exceptional Services to the Society |
| | H. H. BOWEN (Bar) | For Exceptional Services to the Society |
| | Prof. W. BRADLEY | For Exceptional Services to the Society |
| | C. O. CLARK (Bar) | For Exceptional Services to the Society |
| | J. G. GRUNDY | For Exceptional Services to the Society |
| | R. J. HANNAY | For Exceptional Services to the Society |
| | H. H. HODGSON (Bar) | For Exceptional Services to the Society |
| | M. LAPWORTH | For Exceptional Services to the Society |
| | A. THOMSON | For Exceptional Services to the Society |
| | T. VICKERSTAFF | For Exceptional Services to the Society and for Research in the Tinctorial Arts |
| 1959 | I. D. RATTEE | For the Invention and Development of the first Practical System of colouring Cellulosic Fibres with Reactive Dyes |
| | W. E. STEPHEN | For Distinguished Contribution made over many years to International Relations amongst Dyers and Colourists |
| | H. RIS | |

Silver Medal

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|------|---------------------------------|--|
| 1912 | J. H. GARNER | Treatment of Effluents from Dyehouses and Textile Factories |
| 1934 | L. A. LANTZ (<i>Chairman</i>) | Exceptional Services to the Society as Members of the Standardisation of Fastness Executive Committee |
| | S. G. BARKER | |
| | H. H. BOWEN | |
| | P. W. CUNLIFFE | |
| | R. S. HORSFALL | |
| | Prof. B. A. MCSWINEY | |
| | C. C. N. VASS | |
| | C. M. WHITTAKER | |
| 1936 | W. A. EDWARDS | Valuable Services rendered to the Society as Honorary Secretary of the Midlands Section since its inception in 1919 to 1935 |
| 1937 | R. RITCHIE | Devoted and Valuable Services as Honorary Secretary of the Scottish Section for eighteen years |
| 1946 | Mrs. E. CUMMINGS
(née Levin) | For her Valued Services to the Society; by her assistance rendered in the preparation of the first <i>Colour Index</i> ; by her Joint Authorship of a number of Papers published in the <i>Journal</i> of the Society, and as an Abstractor for the <i>Journal</i> of the Society for twenty years |
| | E. RACE | For his Valued Services to the Society as Joint Author of thirteen papers published in the Society's <i>Journal</i> |
| | H. TURNER | In recognition of his Valuable Services to the Society and of his twenty-two years' service as Honorary Secretary of the Huddersfield Section |
| 1947 | C. SCHARDT | In recognition of his Valuable Services to the Society over a period of twenty-four years including Chairman, Vice-Chairman, and member, of the Midlands Section Committee |
| 1948 | C. O. CLARK | For Valuable Services rendered to the Society from 1923 to 1948 |
| | D. B. F. McANDREW | For Valuable Services rendered to the Society as Honorary Secretary and Committee Member of the Scottish Section 1935-1947 |
| 1950 | L. A. LANTZ (Bar) | For Exceptional Services to the Society and to the Tinctorial and Allied Industries in connection with Fastness Tests |
| 1953 | A. W. CARPENTER | For Valuable Services to the Society |

Silver Medal—continued

1954	C. C. WILCOCK	For Exceptional Services to the Society and to the Tinctorial and Allied Industries
1955	H. W. ELLIS	For Valuable Services to the Society as Honorary Secretary of the London Section 1938-1954
	J. G. GRUNDY	For Valuable Services to the Society as Chairman of the Washing Fastness Subcommittee
	K. McLAREN	For Valuable Services to the Society as Honorary Secretary of the Fastness Tests Co-ordinating Committee
1955	J. PORTER	For Outstanding Services to the Society, notably in the Inauguration and the Development of the Northern Ireland Section
	M. E. PROBERT	For Valuable Services to the Society as Chairman of the Bleaching Fastness Subcommittee
	J. V. SUMMERSGILL	For Valuable Services to the Society as Honorary Secretary of the Publications Committee from 1945 to date
	E. WILSON	For Valuable Services to the Society as Chairman of the Alkaline Milling, Burnt-gas Fumes, and Perspiration Fastness Subcommittees
1957	F. ATTACK	For Services to the Society as Honorary Secretary of the Scottish Section 1947-1957
1958	A. W. CARPENTER (Bar)	For Continued Valuable Services to the Society
	R. L. ELLIOTT	For Valuable Services to the Society
	H. TURNER (Bar)	For Continued Valuable Services to the Society
1959	G. G. BRADSHAW	For Valuable Services to the Society and particularly as a Member of the Fastness Tests Co-ordinating Committee and the Publications Committee
	H. F. A. BRASSARD	For Valuable Services to the Society and for the Stimulation he has afforded the Society in many Aspects of its Work
	N. HAMER	For Valuable Contributions in Service to the Society
	J. W. REIDY	For Valuable Contributions in Service to the Society

Bronze Medal

1908	J. B. FOTHERGILL	Treatment of Cotton to Cause it to Resist Direct Dyeing Colours
1953	Miss M. FORBES	For Valuable Services to the Society
	H. R. HADFIELD	For Valuable Services to the Society
1958	Mrs. J. M. FIRTH	For Valuable Services to the Society
	K. MELDRUM	For Valuable Services to the Society
	J. K. SKELLY	For Valuable Services to the Society
	H. W. TAYLOR	For Valuable Services to the Society
1959	W. R. LEIGH	For Enthusiastic Services in the Interests of the Society
	J. RAYMENT	For Enthusiastic Services in the Interests of the Society

**The Worshipful Company of Dyers
Research Medal**

The Medal represents the Arms of the Worshipful Company of Dyers of the City of London, which were granted in 1471. The following is a brief description—

Arms—Sable, a chevron engrailed argent, between three bags of madder of the last, corded or.

Crest—On a wreath three sprigs of the gaintree erect vert, fructed gules.

Supporters—Two leopards rampant gardant argent, spotted with various colours; fire issuing from their ears and mouth proper, both ducally crowned or.

Motto—Da Gloriam Deo.

1—The Dyers' Company offer annually a Gold Medal called "The Worshipful Company of Dyers Research Medal", the award of which is open to the authors of papers embodying the results of scientific research or technical investigation connected with the tinctorial arts submitted to the Society of Dyers and Colourists, and published in the *Journal* of such Society during the twelve months ending on the 30th June in the year for which the Medal is granted, and, in the special circumstance provided for by Rule 6, during the twelve months ending on the 30th June in the year previous to that for which the Medal is granted. If a paper shall be published in two or more parts, then for the purpose of the award of the Medal, all the parts together shall be treated as a paper published in the year in which the final part is published.

2—The Medal will not be awarded to the same person on more than one occasion.

The Worshipful Company of Dyers Research Medal— continued

3— The Society of Dyers and Colourists shall consider the papers available for the Medal and advise the Company as to the merits thereof, and if, in the judgment of the Society, none of the papers is of sufficient merit, the Society may recommend that the Medal be not awarded.

4— The Dyers' Company will award the Medal either to the author of the paper which, in all the circumstances, appears to the Company to show the greatest merit, or, in the event of such paper being the work of an author who has already been awarded the Medal, to the author of the paper next in order of merit who has not already been awarded the Medal, and may, if the Company so thinks fit, refrain from making any award.

5— In the event of a paper being the work of two or more persons, the author shall be taken to be that one of them whose work in the opinion of the Society of Dyers and Colourists has most substantially contributed to the merit of the scientific research or technical investigation embodied in such paper.

6— In the event of the author of a paper of sufficient merit published in the *Journal* of the Society of Dyers and Colourists during any twelve months for which the Medal is awarded being unsuccessful in obtaining the award of the Medal for that period, the Society of Dyers and Colourists may, in their discretion, consider such paper for adjudication with the papers available for the award of the Medal for the next succeeding twelve months.

List of Recipients

1908	Prof. E. KNECHT	A Means of Estimating the Degree of Mercerisation in Cotton Yarns
1909	Prof. ARTHUR G. GREEN	The Chemical Technology of Aniline Black
1910-11	R. L. TAYLOR	The Action of Carbon Dioxide and of Air on Bleaching Powder
1911-12	W. HARRISON	The Electrical Theory of Dyeing
1912-13	S. H. HIGGINS	Observations on the Bleaching of Cotton and The Action of Neutral Salts on Bleaching Solutions
1913-14	W. JOHNSON (in conjunction with Prof. ARTHUR G. GREEN)	The Constitution of Aged and of Bichromate Aniline Blacks
1914-15	MORRIS FORT	The Mechanism of the Acid Dyebath
1915-16	JAMES R. HANNAY	The Interaction between Metallic Copper and certain Dyes of the Thiazine, Oxazine and Azine Series
1916-17	Prof. H. M. DAWSON	The Phenomena of Acid Catalysis and the Theory of Acids
1917-18	L. G. RADCLIFFE	The Sulphonation of Fixed Oils
1918-19	C. F. CROSS (Diplomas presented to M. C. LAMB and C. V. GREENWOOD as co-authors)	Colloidal Tannin Compounds and their Applications
1919-20	A. E. EVEREST (Diploma presented to A. J. HALL as co-author)	The Tinctorial Properties of some Anthocyanins and certain Related Compounds
1920-21	Prof. G. T. MORGAN	The Co-ordination Theory of Valency in Relation to Adjective Dyeing
1921-22	S. JUDD LEWIS	On the Fluorescence of Cellulose and its Derivatives
1922-23	Prof. ARTHUR G. GREEN (Bar) and K. H. SAUNDERS	The Ionamines— A New Class of Dyestuffs for Cellulose Acetate Silk
1923-24	S. JUDD LEWIS (Bar)	The Quantitative Determination of the Fluorescent Power of Cellulose and its Derivatives
1924-25	Prof. F. M. ROWE (with Diploma to Miss E. LEVIN as co-author)	The Identification of Azo Colours on the Fibre and of Azo Pigments in Substance
1925-26	H. H. HODGSON	Behaviour of the Sulphides of Sodium in Aqueous and Alcoholic Media and The Action of Sulphur on the Monochloranilines
1926-27	Prof. F. M. ROWE (Bar) and Diplomas awarded to collaborators— Miss E. LEVIN, A. C. BURNS, J. S. H. DAVIS, and W. TEPPER	A New Reaction of Certain Diazosulphonates derived from β -Naphthol-1-sulphonic acid, leading to the preparation of Phthalazine, Phthalazone and Phthalimidine Derivatives
1928-29	F. SCHOLEFIELD (with diplomas to Miss E. HIBBERT and C. K. PATEL as co-authors)	The Action of Light on Dyed Colours

The Worshipful Company of Dyers Research Medal—continued

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|---------|---|---|
| 1929-30 | H. H. HODGSON (Bar) | Colour and Constitution from the Stand-point of Recent Electronic Theory |
| 1930-31 | Prof. F. M. ROWE (Second Bar) and Diplomas awarded to S. UENO and F. H. JOWETT as collaborators | Insoluble Azo Colours on the Fibre and Action of Boiling Caustic Soda thereon |
| 1932-33 | Two awards—
W. T. ASTBURY

J. B. SPEAKMAN | The X-Ray Interpretation of Fibre Structure

The Structure of the Wool Fibre; its Relation to the Dyeing and Finishing Processes of the Wool Textile Trade |
| 1934-35 | H. A. TURNER and Diplomas awarded to G. M. NABAR and F. SCHOLEFIELD as co-authors | The effect of Reduced Vat Dyes upon the Hypochlorite Oxidation of Cellulose |
| 1935-36 | Prof. F. M. ROWE (Third Bar) and Diplomas awarded to C. H. GILES, R. L. M. ALLEN, W. G. DANGERFIELD, and GLYN OWEN as collaborators | Decomposition of Azo Dyes by Acids, Caustic Alkalis, and Reducing Agents |
| 1936-37 | J. B. SPEAKMAN (Bar) and Diplomas awarded to C. S. WHEWELL and J. L. STOVES as collaborators | The Reactivity of the Sulphur Linkage in Animal Fibres |
| 1937-38 | Prof. F. M. ROWE (Fourth Bar) and J. B. SPEAKMAN (Second Bar) and Diplomas awarded to E. RACE and T. VICKERSTAFF as collaborators | The Uneven Dyeing of Wool with Acid and Chrome Dyes. Part I—The Reasons for the Uneven Dyeing Properties of Wool Staples and of Cloth Damaged by Exposure, and Part II—A Method for Correcting the Uneven Dyeing Properties of Wool Staples and of Cloth Damaged by Exposure |
| 1939-40 | T. H. MORTON as senior author | Application of Vat Dyes to Viscose Rayon, by J. BOULTON and T. H. MORTON |
| 1941-42 | T. VICKERSTAFF as senior author | The Dyeing of Cellulose Acetate Rayon with Dispersed Dyes, by T. VICKERSTAFF and E. WATERS |
| 1943-44 | J. BOULTON | The Importance of Dyeing Rate—an Interpretation for the Practical Dyer of Recent Research on Direct Dyeing |
| 1946-47 | H. PHILLIPS as senior author | The Chemical Constitution and Physical Properties of Bisulphited Wool, by E. G. H. CARTER, W. R. MIDDLEBROOK, and H. PHILLIPS |
| 1947-48 | J. M. PRESTON | Some Factors affecting the Dyeing of Viscose and Some Aspects of the Drying and Heating of Textiles |
| 1948-49 | H. LINDLEY as major contributor | The Mechanism of Set and Supercontraction in Wool Fibres, by S. BLACKBURN and H. LINDLEY |
| 1950-51 | J. CRANK | The Diffusion of Direct Dyes into Cellulose. III—The Present State of the Theory and its Application |
| 1951-52 | H. HAMPSON | Advances in the Application of Vat Dyes to Viscose Rayon Cakes |
| 1952-53 | R. H. PETERS as senior author | The Reduction Properties of Vat Dyes, by W. J. MARSHALL and R. H. PETERS |
| 1953-54 | R. J. HANNAY as senior author | A New Method of pH Control in Dyeing and Some Observations on the Metachrome Process, by R. J. HANNAY, W. H. MAJOR, and R. PICKIN, and The Use of Hydrolysable Esters in the Control of Dyebaths, by R. J. HANNAY and W. H. MAJOR |
| 1954-55 | C. H. GILES as senior author | A Study of Certain Natural Dyes. I—The Adsorption of Brazilwood and Logwood Colouring Matters by Fibres, by F. M. ARSHID, J. N. DESAI, D. J. DUFF, C. H. GILES, S. K. JAIN, and I. R. MACNEAL, and II—The Structure of the Metallic Lakes of the Brazilwood and Logwood Colouring Matters, by F. M. ARSHID, R. F. CONNELLY, J. N. DESAI, R. G. FULTON, C. H. GILES, and J. C. KEPALAS |

The Worshipful Company of Dyers Research Medal—continued

1955-56	C. L. BIRD as senior author	Series of papers on The Dyeing of Acetate Rayon with Disperse Dyes I-V, by C. L. BIRD, Miss P. HARRIS, F. MANCHESTER, and D. F. SCOTT
1956-57	K. McLAREN	Series of papers on Light-fastness Testing and Fading of Dyes
1957-58	A. JOHNSON as senior author	Series of papers on The Chemistry of Esters of Leuco Vat Dyes
1958-59	No award	

The Worshipful Company of Feltmakers Research Medal

The Feltmakers' Company offer annually a Gold Medal for papers embodying the results of scientific research or technical investigation connected with the art of feltmaking and published in the *Journal of the Society*.

Knecht Memorial Fund

A Fund of £100 was subscribed as a Memorial to the late Professor Edmund Knecht. From the interest on this sum two prizes, in the form of books, are awarded annually to selected students of the Manchester College of Science and Technology and the Royal Technical College, Salford.

Mercer Lecture

This lecture was instituted by an anonymous donor in commemoration of the centenary of the discovery of mercerisation.

1944	N. G. McCULLOCH and G. S. HIBBERT	Science in an Old Industry
1945	G. S. J. WHITE and T. VICKERSTAFF	Colour
1946	D. ENTWISTLE	Regenerated Fibres from Natural Polymers
1947	E. J. BOWEN	Colour and Constitution—The Absorption of Light by Chemical Compounds
1948	F. FARRINGTON	Textile Printing
1949	E. WILSON	Some Applications of Chemistry to Textile Finishing
1950	A. B. MEGGY	Some Recent Developments in the Theory of Dyeing
1951	D. TRAILL	Some Trials by Ingenious Inquisitive Persons—Regenerated Protein Fibres
1952	F. C. WOOD	Non-felting Wool and Wool Mixtures
1953	J. R. BLOCKEY and D. H. TUCK	The Coloration of Leather
1954	N. W. YELLAND	Physics in the Dyeing, Printing, and Finishing Industries
1955	G. LANDELLS	Modern Resin Finishing
1956	R. K. FOURNESS	Disperse Dyes—Their Development and Application
1957	J. S. WARD	The Influence of Fibre Types on Dyeing Methods
1959	I. S. MOLL	Aspects of Pigment Dispersion related to Usage

George Douglas Lecture

A sum of £2000 was given to the Society by the Bradford Dyers' Association Ltd., the income from the investment of which is employed in providing a biennial lecture on some subject connected with the colouring or finishing of textiles.

1949	H. LEVINSTEIN	George Douglas, His Times, and Some Thoughts on the Future
1952	R. HILL	Synthetic Fibres in Prospect and Retrospect
1953	T. HOLBRO	The Search for New Dyes in relation to Modern Developments in the Textile Field
1957	G. S. J. WHITE	Dyeing—The Apotheosis of Synthesis or a Team playing for its Colours against White
1958	W. GUTMANN	Textile Finishing—Problems of Today and Tomorrow

Proceedings of the Society

Recent Advances in Textile Printing with special reference to Calcium Sulphoxylate Formaldehyde

R. J. HANNAY

*Meeting of the Manchester Section held at the Textile Institute on 17th October 1958,
Mr. J. W. Reidy in the chair*

A description is given of investigations aimed at producing increased stability of prints containing sulphoxylate formaldehyde reducing agents and avoidance of "haloing" and "wicking" in the production of discharge prints on protein fibres and synthetic fibres such as acetate rayon and nylon.

Introduction

The work described in this paper is partly a continuation of work published in 1953¹, and partly an attempt to solve problems which have arisen due to the rapid increase in the amount of fabric made from man-made fibres which has come forward for printing in the past five years. Two main problems called for detailed investigation, viz.—

- (1) How to increase the stability of sulphoxylate printing pastes to air oxidation under certain circumstances
- (2) How to prevent the "swelling" or "haloing" which occurs when printing pastes containing sulphoxylate reducing agents are applied to a number of man-made fibres which exhibit much more hydrophobic properties than the natural fibres cotton, wool, and silk.

Catalytic Oxidation of Sulphoxylates

The effect of acidity and alkalinity on the stability of sulphoxylate pastes and on their reactions with the fibre in printing were fairly fully described in the previous paper¹. A factor which had not been studied was the effect of the presence of traces of metals in the printing pastes on the rate of degradation and oxidation of the sulphoxylate.

A series of experiments was therefore undertaken, and it was established that the presence of quite small quantities of certain metals—in particular iron and copper—had a very significant catalytic effect in increasing the speed of oxidation of sulphoxylates. In order to determine the practical effect of this type of reaction in textile printing, it is necessary to examine the various stages at which oxidation can take place, as well as the level of concentration of metal which is able to produce a noticeable effect. It was found that as little as 20 p.p.m. of iron or copper under certain conditions affected the stability of print pastes to an appreciable extent, if other conditions were favourable, but a number of factors must operate in order to give rise to any serious trouble. It is comparatively rare for a machine printer to complain of any serious difficulty when printing with ordinary sodium sulphoxylate formaldehyde (Formosul) (C.I. Reducing Agent 2); difficulties are

much more frequently encountered by screen or block printers. The explanation is fairly well known. Once printed goods are properly dried and kept under dry, moderately cool conditions, they are comparatively stable, but if they are dried slowly with warm air with a relatively high humidity, then oxidation of the reducing agent will take place, and the speed at which this occurs is greatly increased by the presence of trace metals. Therefore, the three factors which are involved are humidity, temperature, and exposure to air oxidation.

An examination was made of the effect on the printing paste in bulk. An alkaline Formosul paste containing 100 p.p.m. iron was heated to 70°C. and allowed to cool over 12 hr. The loss of sulphoxylate over a period of 14 hr. was only 3% greater than in a paste containing no added iron. However, if this paste is printed on a fabric and dried slowly in warm air, very rapid oxidation of the sulphoxylate in the printed portion will take place, in 30 min., and can give rise to poor yields and uneven prints. It is possible to prevent this decomposition by adding a sequestering agent, but this addition adds to the cost of the printing paste.

There is now available a special grade of Formosul which has been slightly modified in manufacture and which imparts significantly improved stability to air oxidation to the printed goods during drying. As mentioned earlier, however, so little trouble is normally experienced by roller printers that it is really of interest only to screen printers and block printers who are experiencing difficulty, and even in this field, by careful control of the drying conditions, trouble can be cut down quite considerably when using the ordinary grade of material.

Prevention of Haloing on Man-made Fibres

Early in this investigation it became obvious that a distinction has to be made between what the printers term "swelling" or "haloing" in the case of the natural fibres and the effect obtained on the newer fibres. In the case of the older fibres swelling is largely due to the hygroscopic nature of the printing paste and the condensation which occurs during the steaming process. This effect is usually overcome by modifying the hygroscopic properties of the printing paste and adjusting steaming conditions.

With the newer fibres, swelling or haloing is caused by the capillary attraction of moisture by the hydrophobic fibre immediately the aqueous print pastes come in contact with the fabric. Any soluble salts present in the printing paste are taken in solution along with the water, and when the material is steamed there is sufficient present to give rise to the haloing effect.

Suggestions have been put forward for preventing this effect, e.g. pretreatment of the fabric with some agent which will inhibit the capillary attraction of the water in the printing paste, or addition to the printing paste of a solvent or swelling agent which will produce immediate wetting. Both methods are capable of giving improved results, but both have certain disadvantages. In the first case, pretreatment of the fabric by an agent which inhibits the capillary attraction of water also makes it more difficult to obtain penetration and fixation of the dye in the print paste, or if the print paste is a white discharge it makes it more difficult for the reducing agent to penetrate and discharge the dyed ground. In the second case, the addition of sufficient solvent or "swelling" agent to cause instantaneous wetting generally results in a print paste which is extremely hygroscopic and which will give rise to the older type of swelling in the steaming operation.

After many experiments the conclusion was reached that the only way to ensure maximum safety lay in using a reducing agent which was insoluble in water, and indeed the success of Manofast (Hardman & Holden Ltd.) (C.I. Reducing Agent 11) in avoiding this particular trouble lies entirely in its extremely low solubility in water.

Printing pastes containing a high proportion of insoluble matter have not been very popular with printers, because of a number of difficulties to which many of them give rise, e.g. "sticking-in", scratching of copper rollers, and blocking of screens, but there can be little doubt that, for the type of trouble under consideration, the greatest margin of safety is achieved only by the use of such pastes.

The most obvious material to investigate first was the well-known basic zinc sulphonylate formaldehyde (Zinc Formosul) (C.I. Reducing Agent 4), which is still used to a small extent in the production of discharge prints on silk. This product, however, is very hard, crystalline and coarse, and gives rise to a great deal of trouble, particularly when applied in roller printing. These troubles are not merely connected with the particle size of the product, but are also concerned with its inherent physical properties, and no amount of grinding will completely obviate the difficulties experienced when using it.

The problem, therefore, was to produce a water-insoluble sulphonylate of the right physical properties. Attempts were made to alter the physical properties of the zinc salt by different methods of manufacture, but these were not successful, so attention was turned to the calcium salts. At first similar difficulties were experienced, but it finally proved possible to develop a method

of manufacture which gave an extremely fine, soft, talc-like powder, all of which passed through a 90-mesh sieve and the bulk of which passed through a 300-mesh sieve. The product causes no scratching of copper rollers and is fine enough to pass through the screens without difficulty in screen printing, and when dried on the fabric is of a slightly waxy nature which prevents "flaking"—a trouble which has caused considerable concern among printers when using other insoluble reducing agents. Tests with this product, which is sold under the trade name of *Brotasul*, indicated that excellent results could be obtained, both in discharge printing and in the direct printing of vat dyes on fabrics composed of silk, wool, cellulose acetate, cellulose triacetate or nylon.

Printing with Brotasul

Requests from the industry regarding the production of vat prints and discharge prints on cellulose acetate and on nylon fabrics led to the conclusion that the well-known acid leuco technique was the one to adopt. In a number of instances the normal alkaline technique would not be acceptable, because of the risk of hydrolysing cellulose acetate, whilst if wool were present the fibre would be damaged by the alkaline printing pastes. Experiments showed that excellent results could be produced by means of this technique, both in discharge prints and in direct vat printing. Yields of vat dye on the cellulose acetate and brightness of colour were extremely good, and in the case of wool fabrics no tendering of the fibre was observed. The following are typical standard recipes; they are given as a guide and may need slight modifications to suit local works conditions.

SECONDARY CELLULOSE ACETATE	
STOCK	PRINTING PASTE FOR DIRECT VAT PRINTS ON CELLULOSE ACETATE
60-0	Meypro gum (6%)
12-5	British gum (40%)
15-0	Brotasul
10-0	Polyethylene Glycol 200
2-0	Glydote B
0-5	Teepol, or other similar wetting agent
100-0	

The required amount of vat dye is added to the above standard thickening, which is sufficiently concentrated to accommodate up to 15% of standard vat printing paste. Higher concentrations of dye will probably need a slight increase in the amount of Brotasul, but this can be determined easily by trial.

The above stock recipe is suitable for white or coloured discharges on suitably dyed cellulose acetate in light and medium depths, and may even be suitable for fairly full depths, particularly if 10% of titanium dioxide is added to the printing paste. On heavy shades with dyes which are difficult to discharge it may be necessary to increase the amount of Brotasul to 20% and add zinc sulphate, which increases the discharge properties of the Brotasul. A typical recipe suitable for a white discharge is as follows—

STANDARD RECIPE FOR DISCHARGE PRINTS ON DYED

SECONDARY ACETATE

36-0	Gum Tragacanth (6.5%)
7-0	Titanium dioxide
16-5	Water
5-0	Urea
10-0	Polyethylene Glycol 200
10-0	Zinc sulphate
15-0	Brotasul
0-5	Teepol
100-0	

If coloured discharges are required, up to 15% of vat dye may be added with excellent results, although it will frequently be found that the first recipe, when containing vat dye, will give quite satisfactory results.

NYLON

In general, the recipe given for the production of direct vat prints on secondary cellulose acetate will be found suitable for nylon. For vat dye discharge prints, the addition of zinc sulphate has been found to give improved results. A standard recipe is as follows—

STANDARD RECIPE FOR VAT DYE DISCHARGE PRINTS ON DYED NYLON

34-0	Gum Tragacanth (6.5%)
12-0	British gum (1:1)
14-0	Water
10-0	Polyethylene Glycol 200
2-0	Glydote B
10-0	Zinc sulphate
0-5	Teepol
17-5	Brotasul
100-0	

The vat dye is added to this standard discharge paste as required.

The following recipe is suitable for white discharges—

STANDARD RECIPE FOR WHITE DISCHARGE PRINTS ON DYED NYLON

36-0	Gum Tragacanth (6.5)
7-0	Titanium dioxide
14-0	Water
5-0	Urea
10-0	Polyethylene Glycol 200
10-0	Zinc sulphate
17-5	Brotasul
0-5	Teepol
100-0	

CELLULOSE TRIACETATE

The printing of fabrics woven from Tricel (Courtaulds) presents rather more difficulty, due mainly to the hydrophobic nature of this fibre, which results in insufficient swelling for ready access of dye. Whilst reasonably good results were obtained with recipes similar to those given above for the direct printing of vat dyes, the colour yield obtained on Tricel fabrics was very poor, as compared with yields given on the other two fibres. A fairly exhaustive set of trials with different types of carriers—mainly those recommended for use in dyeing—indicated that little improvement in yield could be obtained. The main exception was

Carrier LB (Courtaulds), which did give significantly increased colour yields, but even so the yield was still well below that which would normally be expected. Further work, however, indicated that greatly increased yields could be obtained by using zinc thiocyanate as a swelling agent in the print paste, and for direct prints the best yield was obtained by using the following technique—

STOCK PASTE

10-00	Vat Dye
14-00	Urea
8-25	Polyethylene Glycol 200
55-00	Gum Tragacanth (6.5%)
12-75	Water
100-00	

PRINTING PASTE

72-5	Stock paste
7-2	Brotasul
10-0	Zinc thiocyanate
10-3	Water
100-0	

The main difficulty with this recipe is that a very careful selection of dyes is necessary, as zinc thiocyanate affects the shade of a number of vat dyes—even of those which are known to be suitable for application by the ordinary acid leuco technique—so the number of suitable dyes is at present limited.

Good white discharges, however, may be obtained on dyed Tricel without the use of zinc thiocyanate, and very good results were obtained on four heavily dyed fabrics with the following recipe—

RECIPE FOR WHITE DISCHARGE PRINTS ON DYED TRICEL

26-5	Gum Tragacanth (6.5%)
10-0	British gum (1:1)
7-0	Titanium dioxide
14-0	Water
10-0	Polyethylene Glycol 200
2-0	Glydote B
10-0	Zinc sulphate
0-5	Teepol
20-0	Brotasul
100-0	

Carrier LB (10%) was added to the above print paste before use.

WOOL AND SILK

Brotasul can also be used in the printing of wool and silk, and excellent results have been obtained in practice. The main interest on wool is in the production of discharge prints, and the following recipe has proved satisfactory for the production of discharge prints on wool dyed black, nigger brown, bottle green or maroon—

RECIPE FOR DISCHARGE PRINTS ON DYED WOOL

32-0	British gum (1:1)
10-0	Zinc sulphate
23-5	Water
10-0	Polyethylene Glycol 200
20-0	Brotasul
4-0	Diethyl tartrate or ethyl lactate
0-5	Teepol
100-0	

The addition of diethyl tartrate or ethyl lactate is not essential, but it helps in obtaining the clearest whites, particularly where the dyed ground has been produced with metal-complex dyes; it also prevents tendering of the wool. Coloured discharges may be produced by incorporating suitable dyes which withstand the reducing action of sulphonylates.

Pigment Discharge Prints

Whilst this work was in progress, work of a similar nature was reported by Bernardy and Wirth², who described a new product suitable for the production of coloured discharge pastes incorporating some of the newer pigment printing emulsions, e.g. the Helizarine dyes (BASF). This product, *Rongalite H* (BASF), is claimed to be completely compatible with pigment printing emulsions containing emulsified resin binders, whereas soluble reducing agents, e.g. *Rongalite C* (BASF) and Formosul, cause difficulties due to the breakdown of the emulsion. This is understandable, since these emulsions, when loaded with electrolytes, in particular strong reducing agents, are normally completely broken down. The fact that *Rongalite H* is compatible with emulsion pigment-printing pastes is due to its insolubility.

Examination of *Rongalite H* has shown it to be very similar to Brotasul and, in fact, the two products can be interchanged in this particular process.

The Triethanolamine Technique

In 1958 Bernardy and Wirth³ recommended the use of *Rongalite H* when applying vat dyes and producing discharges on these fabrics. An alkaline medium is recommended in order to widen the range of suitable vat dyes, but the alkali used is triethanolamine instead of the usual sodium carbonate or potassium carbonate, this substitution enabling cellulose acetate to be printed without saponification. This technique appears to have no significant advantage over the acid leuco method when printing fabrics composed of only one type of fibre, but certain advantages are obtainable when printing fabrics woven from blended yarns containing mixtures of cellulosic fibres and man-made fibres. In such cases the acid leuco technique would give no fixation whatsoever on the cellulosic fibre, but the inclusion of triethanolamine in the print paste enables a reasonably good fixation to be obtained on the cellulosic fibre, without detriment to the fixation and yield on the man-made fibre, thus giving coverage of the two fibres with one dye of high all-round fastness properties.

An example of the usefulness of this particular technique may be cited. A printer was processing a heavy fabric consisting of a cellulose acetate warp and a cotton-covered elastic weft. It was required to print this fabric for the swim-suit trade, in a blotch design with vat dyes. The first attempt employed the normal potassium carbonate-Formosul method. Where the vat dye was properly fixed excellent yield and coverage was obtained, but as the fabric was a heavy one and as the design was extremely heavy and the print a screen print, drying proved to be difficult, with the

result that considerable unevenness occurred, due to loss of reducing agent in patches. The acid leuco technique could not be used, but the difficulty was overcome by using Brotasul with a triethanolamine addition, and although it took ca. 30 min. to dry the final print with warm air blowing direct on to the face of the printed fabric, no loss of reducing agent or unevenness occurred.

The yield of vat dye obtained on the cellulosic fibre by this technique is not as high as that which would be obtained by the normal potassium carbonate- or sodium carbonate-Formosul method, but it is of the order of 66-70%, and, in view of the good yield on the man-made fibre, the result is satisfactory from the economic point of view.

The growing use of blends of synthetic fibres with cotton or viscose rayon makes this particular technique of increasing interest, in particular in those cases where the use of sodium carbonate or potassium carbonate is undesirable. Good results have been obtained on union fabrics composed of yarns of secondary cellulose acetate and cotton, cellulose triacetate and cotton, and nylon and cotton.

The following recipe may be used as a basis, although the proportion of Polyethylene Glycol 200 may have to be decreased, especially if steaming conditions are very moist, or according to the weave, denier and proportion of the hydrophobic fibre present.

STANDARD PRINTING PASTE FOR TRIETHANOLAMINE

	TECHNIQUE
47.0	Meypro gum (6%)
12.5	British gum (40%)
10.0	Polyethylene Glycol 200
5.0	Glydote B
15.0	Brotasul
10.0	Triethanolamine
0.5	Teepol
100.0	

The required amount of vat dye is added to the above paste and printing is carried out in the normal manner. For discharge effects the proportion of Brotasul will probably require to be increased to 20% if the ground shades are heavy.

Summary

The acid leuco technique provides a method of fixing vat dyes satisfactorily on a number of man-made fibres, as well as on protein fibres, without damage to the fibre. It can be employed with sodium sulphonylate formaldehyde (Formosul) or normal zinc sulphonylate formaldehyde (Redusol Z) (C.I. Reducing Agent 6), but extremely accurate control is required, and the narrow margin of safety when using these compounds in this manner involves considerable risk.

The second method employs formamidine sulphinic acid (Manofast) as the reducing agent. This technique has achieved considerable success, but it still has a number of drawbacks, and considerable care is necessary if satisfactory results are to be regularly obtained. In the presence of moisture—and therefore in aqueous printing pastes—Manofast is very sensitive to heat, and if

at any period during preparation the temperature of the printing paste rises above 35–40°C., there is considerable risk of decomposition taking place. Its heat sensitivity is still apparent in the printed goods before they are dried, so the temperature must not rise above 35–40°C. before the print is thoroughly dried. Freshly prepared printing pastes containing formamidinium sulphonic acid develop a pH of 2–3 within 30 min. As the product is unstable when alkaline, neutralising rapidly increases the risk of instability. Considerable "flaking" trouble has been experienced by printers using Manofast, and this has caused an undesirably high percentage of rejects.

On the other hand, the heat stability of Brotasul in aqueous media is very good, and the precautions which have to be taken when using Manofast are unnecessary. In the absence of any added alkali, the pH of printing pastes containing Brotasul—assuming that neutral thickeners are used—lies between 7 and 8 when freshly made and will not fall below 5 even after keeping for 3 weeks, which makes the handling of them much safer and easier and lessens the risk of corrosion. In addition, as the product is stable to alkali, it is possible to add an alkali such as triethanolamine in order to achieve fixation of vat dyes on any cellulosic fibres which may be present.

Owing to the physical nature of Brotasul, "flaking" troubles have not been experienced, even when printing discharges on silk and wool dyed in full depths. One of the main characteristics of Manofast is its stability once it has been successfully printed and dried, and in this respect Brotasul compares very favourably. Thus prints have been kept for as long as 3 weeks before steaming without loss of yield; but such a lengthy period is not recommended and, in general, 3–4 days storage should be considered a maximum. The stability of prints before steaming is much greater when using Brotasul than when using the traditional soluble sulphonylates.

* * *

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(MS. received 23rd June 1959)

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- ¹ Hannay and Furness, *J.S.D.C.*, **69**, 596 (1953).
- ² Bernardy and Wirth, *Melliand Textilber.*, **38**, 1044 (Sept. 1957).
- ³ Idem, *ibid.*, **39**, 292 (March 1958).

Discussion

Mr. A. S. FERN: Is it possible, using Brotasul, to obtain a range of vat prints on nylon possessing a higher light-fastness than is produced by the best

available disperse dyes? Is any information available on the state of the vat leuco compounds when printing with calcium sulphonylate formaldehyde? Are there any vat dyes which are difficult to process by this method, possibly owing to the formation of an insoluble calcium leuco derivative? Can Brotasul be used with thickenings containing sodium alginate?

Mr. HANNAY: The fastness to light of vat dyes on nylon printed by the Brotasul method is similar to that obtained by normal methods of application, but selection of the dyes is required in order to achieve the best standards. *All-round* fastness for branded goods is difficult, and in some cases impossible, to obtain when using disperse dyes, but the necessary standard can be obtained with selected vat dyes. We have not made a study of the state of the vat leuco compounds when using calcium sulphonylate formaldehyde. Work was confined to the application of vat dyes known to be applicable by the acid leuco technique, and excellent results were obtained. Sodium alginate is not recommended as a thickener when using Brotasul.

Mr. A. N. RUSSELL: Is Brotasul stable in presence of trace metals?

Mr. HANNAY: Yes, provided that the metallic contamination is restricted to reasonable limits such as might be experienced by contact with copper printing rollers or steel doctors. In the presence of even 100 p.p.m. iron the stability of the new product is superior to that of normal sodium sulphonylate formaldehyde.

Mr. C. W. SEELEY: Has the lecturer any information as to the comparative fastness to rubbing on hydrophobic fibres of pigment prints and vat dye prints applied by the Brotasul method?

Mr. HANNAY: Tests on the rubbing fastness of vat prints on both secondary cellulose acetate and nylon were carried out by one of our customers. The results were entirely satisfactory. In the case of pigments, the results obtained in another series of tests showed that the method gave a similar fastness to that obtained by normal direct printing methods, but some rubbing did occur, as is usual with all pigment prints, and in this respect vat dyes are superior.

Mr. W. C. MCKNIGHT: Is there any degradation and fall in pH during running in a printing machine?

Mr. HANNAY: No, provided that the print paste has been prepared with a neutral thickening. The pH of a freshly prepared Brotasul printing paste is about 7–8, and it usually takes many days for it to fall to 5. This fall in pH is accompanied by slight oxidation, but the loss in sulphonylate is comparatively small.

A MEMBER: Is Brotasul more difficult to remove in washing and does it retard reoxidation of the vat dyes, with a consequent loss of yield? Does residual Brotasul affect the handle or properties of the material?

Mr. HANNAY: No greater difficulties are experienced in after-processing when using Brotasul with vat dyes than is usual with any other acid leuco technique. There have been no complaints indicating that the product affects the handle of the material.

COMMUNICATION

How much Research?

A Critical Problem in the Manufacture of Textile Dyes

G. S. J. WHITE

A brief review of the history of synthetic dyestuffs manufacture reveals how important "ease of application" has been as a target for research. Resistance to washing and light is an historical part of the art and science of dyeing, and over the centuries has been absorbed by dyemakers into their essential testing and evaluation procedures. The main problem for the dye manufacturer now is the likelihood of reduced reward for speculative research.

In order fully to understand the research problem of the synthetic-dye manufacturer, it is valuable to consider briefly the history of the past 102 years since Perkin founded the industry. At the centenary celebration in Britain, a review was made by four authoritative speakers and is now available in collected form¹. For those who are not of the industry but are concerned in how it has developed, this book will provide an introduction; and to this may be added the proceedings of a symposium recently held by the Manchester Section of the Society on the centenary of Peter Griess's discovery of the diazo reaction². There is, however, another and more dramatic way of presenting this century of progress in synthetic-dye manufacture, and that is by inspecting the newly-published Second Edition of the *Colour Index*. This important work describes the individual commercial dyes, together with their properties and application, in summary form in Volumes I and II; and in Volume III gives the formulae, methods of preparation and references to the discoverers, and chemical processes of manufacture. Volume III includes some 3,500 separate chemicals as dyes, and it can be said that these are the products which have not only reached commercial production but have survived in a highly competitive world. Nearly all of them are currently available from the integrated selling range of world dyestuff manufacture. Of the 600 pages or more devoted to dyes in Volume III, half describe products which can be made by way of the diazo reaction discovered by Griess. I am credibly informed that these 2,000 commercial dyes represent a selection from a total of about a million azo dyes which have been made in the many research laboratories serving the industry. Pondering the need for all this variety reveals one of the problems which confronts dyemakers.

The *Colour Index* shows some 25 chemical classes of dyes, including the aforementioned azo compounds. How did this complexity arise? In Table I the classes are sorted into something a little more understandable by the dye user, and an attempt has been made to divide their origins into two themes. One of these I have entitled "Targeted Research" and the other "Chemical Miracle".

Looking briefly through the table, a "chemical miracle" describes Perkin's original discovery. The credible story is that he was looking for a synthetic route to quinine when the mixture of chemicals he was using united in a special and impressive way to form the purple compound which he then, in a

TABLE I
Possible Origin of Dye Class or Dyeing Method

	Chemical Miracle	Targeted Research
Perkin's Mauve	×	
Griess's diazo reaction	×	
Azo direct cotton dyes		×
Vacanceine Red		×
Sulphur dyes	×	
Vat dyes	×	
Chrome dyes		×
Azoic (improved ingrain)		×
Soluble vat dyes		×
Disperse dyes		×
Metal-containing azo dyes		×
Phthalocyanines	×	
Reactive dyes		×

flash of inspiration, showed to be a dye for silk. The second title of "chemical miracle" can rightly be attributed to the diazo reaction. A prior study of the reactants could not have foretold that colour would be the chief property of the products of the reaction. The diazo reaction has been the great inspiring river of colour chemistry that has run through the whole hundred years of our history down to the present day, when its application not only continues in manufacture, but shows itself again in the latest invention of the dye chemist: the new range of "reactive" dyes.

With some reservations, sulphur dyes are treated as a chemical miracle, the reservation applying to the chemical nature of the reaction rather than to the economic and practical value of the products derived from it. In the next example, there is no doubt at all that René Bohn's discovery of indanthrone was another chemical miracle, since he is said to have been looking for an alternative route to indigo when he was surprised by the dyeing properties of the product of his chemistry. After indanthrone, the industry had to wait 30 years for the miracle of phthalocyanine. This product appeared from the reaction of phthalonitrile with copper salts and unexpectedly gave a very stable blue compound, insoluble in water and highly resistant to light and solvents. This pigment has since been chemically treated to provide a number of outstanding textile dyes.

Studying Table I, it is noteworthy that chemical miracles seem to occur with great infrequency and at approximately 30-year intervals, and this despite the enormous teams of highly skilled manpower researching in the field. It is also noteworthy that the versatility of these chemical

discoveries appears to have fallen from the highly versatile diazo reaction to the very much less versatile sulphur dye, increasing again a little with the extended range of vat dyes. These currently available vat dyes, resulting from 50 years of chemistry, now effectively cover an appreciable part of the colour solid, but appear almost to have reached their limit in colour development. Phthalocyanines provide a range of bright blues and greens, but within the compass of their intrinsic chemistry show this very marked degree of spectral limitation.

In the third column of Table I which I have specified as "targeted research", there is shown first the industry's achievement of the direct cotton dye Congo Red, discovered by Böttiger in 1884. This occasion must have been a very exciting event indeed. Up to that time, organic-dye chemists had used the variety of the reactions they had discovered only to provide them with coloured compounds, without any discrimination as to their use. It had been the chemists and technologists of the industries concerned with their application, and mainly those in the textile industry, who evaluated and established whether these new dyes had uses in their own particular fields. Some of the dyes evolved in that era are still in use today, generally not in the textile industry, as their properties have been surpassed by those derived from the targeted research of subsequent years. Böttiger's investigations leading to the synthesis of Congo Red were the first clear-cut successful fulfilment of a research target which had only been appreciated for a short time. The next item under this head which is worthy of mention is the "ingrain" dye passing under the trade name of Vacanceine Red. The inventors clearly had in mind the lack of fastness to washing on cotton of the azo dyes, which were until then only produced either as basic dyes or as water-soluble sulphonates. The defects in application of Vacanceine Red and the closely related Para Red later inspired Zitscher and his co-workers, in 1911, and led to the Naphtol range. These dyes have established the ingrain technique as one of the great contributors to fast colours, and incidentally as a further example of the versatility of the diazo reaction.

Early in the century, synthetic water-soluble chromable dyes for wool were produced, and this too must have been the result of targeted research, for the process of mordanting with metal salts was well known to dye users prior to the synthetic age. After the first World War, difficulties in the application of vat dyes made it possible for the research chemist to devise the soluble vat dyes, with their hydrolysable and labile sulphate groups which can be removed after the dyes have been applied to the cloth, leaving the insoluble vat dye embedded in the fibre with all its pristine resistance to washing treatments. I have also classed the discovery of the disperse dyes for acetate rayon as targeted research. Although some of the dyes made for the purpose were novel, the objective was clear, distinct and different from all the other current problems of textile dyeing.

The clever idea of including the metal of the

mordant—chromium or copper—in the dye molecule itself was certainly a target for chemical research, and was brilliantly solved in or around 1920. The last major discovery in dye application, that of the reactive dyes, was also the fulfilment of a clear research objective, which was to unite the dye chemically with the fibre. This problem had challenged the dye chemist for many years, and the first commercially available range was a fitting centenary celebration for the synthetic dye industry.

This brief and cursory review is intended to show two things: firstly the infrequency with which an organic chemical reaction unexpectedly yields a coloured compound of value in application; and secondly the importance of appreciating the needs of the dye-using industry, and particularly the textile dye-using industry, and so being able to define the targets for dyes with properties of colour, application, or fastness not hitherto available.

What now are these broad targets for research and needs for new dyes for textiles? Without making the subject too complicated by defining in detail the types of resistance which are demanded of dyed fabrics, both in processing and in ultimate use, it is possible to summarise the needs under three headings: firstly ease of application, secondly colour fastness, and thirdly colour gamut.

The first two needs are self-explanatory, but "colour gamut" may require a little definition. It was recognised that many of the first synthetic dyes to be discovered (basic dyes) were far brighter than most natural dyes, and it was this brilliance of hue that was their initial attraction. The diazo reaction, versatile chemically, proved to have restrictions in the field of colour, being useful for reds, oranges, yellows, navy blues, and blacks, but lacking bright greens and blues. Vat dyes have greens and blues of intermediate brightness, but even today are defective in bright reds, scarlets and yellows of outstanding fastness properties. As already mentioned, the phthalocyanine reaction yields blues and greens of high colour value and brightness, but is very much restricted to this section of the colour solid. Many will recall a paper by Vickerstaff³ given to the joint meeting of

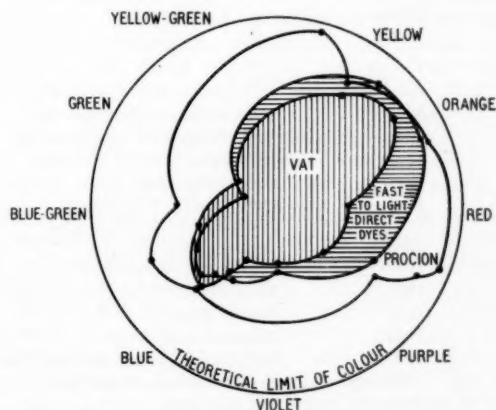


Fig. 1—Colour gamut of reactive dyes as compared with those of direct dyes and vat dyes

the Textile Institute and the Society of Dyers and Colourists at Scarborough in 1954. Here was displayed for the first time the comparative extent to which the then-known ranges of commercial dyes provided a volume of colours in the hypothetical colour solid. To complete the present-day picture, Fig. 1 provides a comparison between the colour gamut of the present range of reactive dyes and those of the vat and direct dyes.

To generalise on the subject, it would seem advantageous for a chemical class of dyes to produce the largest range of colours possible whilst maintaining the fastness characteristics of its technological group. Some of the purpose of dye-stuff research hitherto has been to supplement shortages in fast-colour ranges by individual items differing chemically from the main chemical theme of the class. An example of this is the use of the "onium" type of Phthalocyanine Turquoise which, when applied to cotton by printing or by piece or yarn dyeing, is of vat fastness so far as the ultimate consumer is concerned, and it can be applied alongside vat dyes in ranges of fast-to-washing goods, the anthraquinone vat dyes being quite devoid of turquoise colours of this brightness.

Let us return now to consider the importance of the other two principal needs of the dye user, which were defined above as "ease of application" and "colour fastness". It will assist us in getting these problems into perspective if we again look back to the history of the development of commercial dyestuffs and take as our example those derived from the diazo reaction, which amount to more than one-half of all the commercial dyes. Table II purports to display which was the primary objective of the various discoveries and inventions so far as textile colouring is concerned. The three objectives dealt with in Table II are (a) increased colour fastness, (b) special application, and (c) ease in application.

The first two inventions seem to have had no special objective, but the first direct cotton dye can clearly be classed under "Special Application". Vacanceine Red had as its primary objective increased colour fastness. Products which were

designed for easier application were the stabilised diazo compounds, metachrome dyes, azoic dyes, the ranges of azo dyes presenting both stabilised diazo compound and colour coupler together—originally referred to as the *Rapidogen* and *Rapid Fast* ranges—Neolan dyes (the first metal-complex range), and some of the special dyes for new fibres. Other ranges of azo dyes were the chrome dyes, which clearly were aimed at increased colour fastness; some of the disperse dyes, which were designed for special application; some of the dyes for new fibres which had increased colour fastness as their objective; and the Procion dyes, which share increased colour fastness and easier application.

In considering Table II, it must be understood that the classification applies only to the first member of the new range and not to any subsequent proliferation. Although the later work has been of the greatest technical importance to the dye user, the aim in Table II is to define the targets which have hitherto been set up and attacked more or less successfully by the dyemaker. This tabular summary seems to indicate clearly that most attention has been devoted and most success has been achieved in making products easier to apply than those which were available at the time of the invention, and that colour fastness has also had an important place as an object of textile dye research.

That this is so should not surprise us greatly. Fig. 2 displays in a formal and rationalised manner the two-way technical communication from the dyemaker at the head of the table through the textile dyer and printer, his merchant converter, an abbreviated range of wholesaler, maker-up, wholesaler, retailer, to the ultimate consumer.

The technical communication from the dyemaker to the textile dyer and printer has been cultivated by both parties over the whole history of synthetic-dye manufacture. Both parties have employed chemists and technologists and have laboratories for evaluation and testing, which have had somewhat different commercial aims, but which approach the problem of the properties of dyes on fibres with identical technical objectives.

TABLE II

Date	Event	Primary Objective in Textile Colouring		
		(a) Increased Colour Fastness	(b) Special Application	(c) Easier Application
1858	Azo reaction first discovered		No special objective	
1863	First commercial dye available		No special objective	
1876	First water-soluble anionic dye		No special objective	
1880	Vacanceine Red	×		
1884	First direct cotton dye		×	
1894	Stabilised diazo compounds			×
1902	Chrome dyes	×		
1903	Metachrome dyes			×
1911	Azoic dyes			×
1920	Neolan dyes			×
1923	Disperse dyes		×	
1925-30	Rapidogen and Rapid Fast dyes			×
1950 approx.	Nylon and new-fibre dyes	×		
1956 approx.	Reactive dyes	$\frac{1}{2} \times$		$\frac{1}{2} \times$
Total		$3\frac{1}{2}$	2	$5\frac{1}{2}$

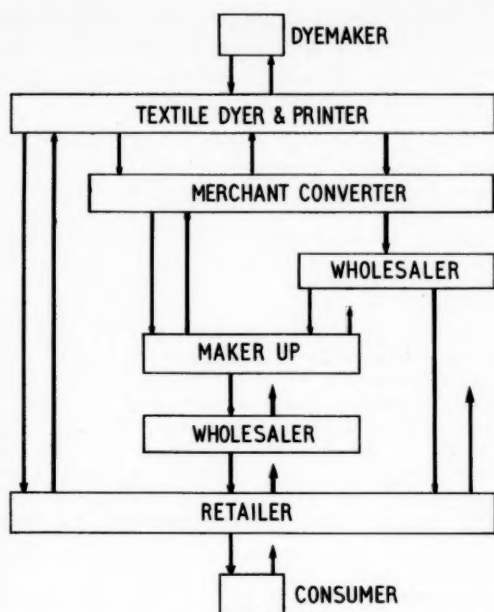


Fig. 2—Conventional pattern of communication from dyemaker to ultimate consumer

These technologists speak the same technical language and confer together in many successful societies over the world, among which the Society of Dyers and Colourists is rightly proud to be a leader. Dyemakers have valued this close contact greatly, and from their own laboratories pour out a flood of technical information concerning the properties of the products they manufacture and market, based on tests simulating the practices of the using industries.

Having now established that an excellent two-way communication exists between the dyemaker and the user of his products, let us glance at the nature of the contact with the ultimate consumer. He or she, when purchasing coloured cloth or garments, will have two important guides as to their quality. The first is the reputation of the retailer, and more particularly his attitude in controlling or not the quality of the dyed or printed materials which he sells. A small number of important retailers do this in an authoritative manner and accept the principle that the colour of the goods should last as long as the fabric is serviceable. In addition to this valuable aid, the consumer has the advantage of the house brands and labels of established manufacturers and converters. Here the British manufacturer has pioneered the label with the sound reputation, but in some parts of Europe and in the rest of the world there has been less attention by textile manufacturers to the importance of ensuring that the quality of dyed goods is satisfactory. Because of this and during the period between the two World Wars, the sections of the German dyestuff manufacturers who made vat dyes decided to popularise a brand mark of their own for cotton fabrics which were coloured to certain high standards of light- and washing-fastness. They spent large sums of

money in establishing the *Indanthren* label, which carried with it the implication of a guarantee of quality. This met with considerable resistance from the textile manufacturers on the Continent, to such a degree that the subordinate company of the dyemakers responsible for the label had to establish retail shops displaying and selling cloth and garments carrying their label, thus ensuring that it would reach the public and be associated in the minds of the purchasers with goods of a high standard of fastness to washing and light. All this activity was halted by the second World War and for a period after the war. However, by 1950, when supplies of textiles were beginning to be more freely available in all the countries of Western Europe, there was an increasing cry from the public for a reinstitution of this label; the call was particularly clear in Norway and Holland, but was also encountered in many other countries. Because a wider interest than that previously involved was apparent, an international committee was set up to examine the possibility of establishing an acceptable and recognisable label without limitation as to the dye-maker or -user. The history of the establishment of the *Felisol* label has been described by McLaren⁴. The label is controlled by the international committee of dye-users and -makers, who have set up a technical body which tests and accepts dyes and dyeings as worthy of the *Felisol* label. The results of these agreed tests are displayed in the *Felisol* publications of the individual dyemakers. It is noteworthy that in Britain there appeared to be very little use for this type of label before the war, which confirms the widespread public acceptance of the brand marks of individual textile manufacturers and the quality of goods bearing those marks. The British textile trade exporting to Europe will, however, have to take some heed of the publicity and excellent technical backing which have been brought to a point of recognition in the *Felisol* label.

It might appear, from what has been stated above, that the ultimate consumer is in an entirely satisfactory position. Personal experience leads us all to believe that this is not so. Let us turn back to Fig. 2, which illustrates the two-way communication between the parties involved in carrying dyes on dyed and printed materials to their ultimate consumer. All seems well in the communication down the chain, although how technically satisfactory is difficult to appraise, but all may not be so well on the return journey. A measure of this difficulty has been stylised in the diagram, in that some of the arrows showing the return of consumer information are made short.

Where washing fastness of the goods is at fault and the consumer complains, the best retailers will request some information about the types of detergent employed. They will properly query whether the temperature and time of washing have been reasonable or whether by mistake some bleaching liquor has been added, resistance to which was not to have been expected. Having culled this information, they will then confront the ramification of intermediaries between them and the dyer or printer, and at each stage they will

generally not be concerned with technical folk, but with commercial people who will endeavour to settle the complaint by substitution of other goods or cash payment, and so severs the chain of technical communication. Where the means of communication are excellent, as in those cases of dyers and printers who own or control retail shops—a practice more common outside Britain than within—the satisfaction of the ultimate consumer becomes very much more within the control of the dye user. Twice in the recent history of the Manchester Section of the Society, the subject of colour fastness has been debated before an audience including several ladies who were clearly dissatisfied with what is being done to control the quality of the colour of all the goods sold to the ultimate consumer.

If this unchallenged picture displayed by those ultimate consumers were freely accepted, the dye-making industry might be forgiven for assuming that there were still great unsolved problems of colour fastness as targets for research. It is very

doubtful whether this is so, but let us examine the dimensions of the problems as it concerns resistance to washing. The whole colour gamut of dyes and their resistance to washing can be exemplified in brief, as shown in Table III.

Table III shows six common textile fibres and four degrees of resistance to detergents. It is clear that a high degree of washing fastness is possible on all these six fibres, and, in addition, on the older and more commonly used materials, there are products of excellent all-round resistance to bleaching and light as well as to detergents.

Table IV shows what limitations there are in the colour gamut which is possible, and sets this out as a relationship between colour gamut and washing fastness. Three volumes within the colour solid are referred to as—a wide range (3), a somewhat restricted range (2), and a very restricted range (1). All the fibres save nylon and Terylene show that a wide range of shades is possible, not only in low or medium degrees of washing fastness, but also in colours of high fastness and excellent

TABLE III
Resistance to Repeated Domestic Washing

	Low Fastness	Medium Fastness	High Fastness	Excellent All-round Resistance
Wool	Level dyeing acid dyes	Metal-complex and milling acid dyes	Metal-complex and milling acid dyes	Chrome dyes
Nylon	Disperse dyes	—	Speciality and acid wool dyes	—
Cotton	Direct dyes	Sulphur dyes	Reactive dyes	Vat and azoic dyes
Resin-treated viscose rayon	Level dyeing direct dyes	Aftertreated direct dyes	Reactive dyes	(Vat) azoic dyes
Acetate rayon	Disperse dyes	—	Azoic dyes	—
Terylene	—	Disperse dyes	Azoic dyes	—

TABLE IV
Colour Gamut Relative to Wash Resistance

	3—Wide Range	2—Somewhat Restricted	1—Very Restricted	
	Low Fastness	Medium Fastness	High Fastness	Excellent All-round Resistance
Wool	3	3	3	1
Nylon	2	—	2	—
Cotton	2	1	3*	2
Resin-treated viscose rayon	2	2	3*	2
Acetate rayon	3	—	1	—
Terylene	—	2	1	—
Average	2.4	2	1.75 (2.16*)	1.66

* Reactive dyes included

TABLE V
Ease of Application relative to Wash Resistance

	3—Easiest to Apply	2—Average	1—Difficult	
	Low Fastness	Medium Fastness	High Fastness	Excellent All-round Resistance
Wool	3	2	2	1
Nylon	3	—	2	—
Cotton	3	2	3*	1†
Resin-treated viscose rayon	3	2	3*	(1)
Acetate rayon	3	—	1	—
Terylene	—	1	1	—
Average	3	1.75	1.5 (2*)	1

* Reactive dyes included

† Soluble vat dyes omitted

all-round resistance, except in the case of acetate rayon and Terylene, where the range is somewhat restricted. That a wide range of colours is obtainable on cotton and viscose rayon now is attributable to the new degree of brightness possible with reactive dyes.

Table V shows the relationship between ease of application and washing fastness for the same fibres. If the reactive dyes on cotton and viscose rayon are omitted from the overall picture, it is seen that there is a direct relationship between ease of application and resistance to washing. On all the fibres, low fastness is accompanied by ease of application, whereas on five fibres, high fastness to washing involves difficult application conditions. The degrees of difficulty vary from those associated with the application of azoic dyes to Terylene, where the low rate of dyeing and penetration of the fibre calls for high temperatures and long dyeing times, to the difficulties of colour matching when mixtures of chrome dyes are applied to wool. The reactive dyes, when included, alter the balance toward easier application in the category of high resistance to washing. However, they are in the early stages of their practical development and use, so it is not possible to be in as definite agreement about their dyeing and printing properties as it is with the older types of dyes.

From this examination it seems likely that, to the dyer and printer, the application of dyes of high fastness will call for increased processing and greater control than the techniques which produce satisfactory results with dyes of lower fastness, and this must make the result somewhat more costly. To this must be added a measure of the increased cost that may be derived by the difficulties accompanying the synthesis of the faster dyes.

As an example of these two contributory factors, let us consider three ways of producing a bright turquoise colour by using a substituted phthalocyanine molecule on cotton cloth. Copper phthalocyanine is insoluble in water and organic solvents and, in order to make it suitable for dyeing cotton, a number of different chemical reactions are performed upon it. The first and simplest is to sulphonate it by a treatment with sulphuric acid. This produces a direct cotton dye. The second and more complex procedure is to attach a side chain to the phthalocyanine structure and to quaternise the side chain with a substituted amine so that a water-soluble cationic dye is formed: the "onium" dye. The third and most recent method is to attach a side chain to the phthalocyanine molecule and to this side chain append a group or groups containing labile and "reactive" chlorine atoms. The three dyeings, when examined, show

very little difference in colour and appearance, but the processes of dyeing progress from easy in the case of the simple sulphonated direct cotton dye, through the reactive dye in an intermediate position, and then to the "onium" compound which, whilst not difficult in itself to dye, requires careful cloth preparation to give a good level result (see Table VI).

TABLE VI
Phthalocyanine Turquoise

	Ease of Application	Ease of Synthesis	Fastness to Detergents
Sulphonate (direct dye)	3	3	Low
Reactive	2	2	High
"Onium"	1	1	Excellent all-round

If further example is necessary, then consider the case of a representative reactive dye, which can be expressed chemically as a coloured molecule attached to a cyanuric chloride ring, the latter group being responsible for the chemical attachment of the dye to the fibre, so giving it good washing resistance. This cyanuric chloride ring makes very little contribution to the colour of the resultant dye, but is an appreciable part, some 15-20%, of the weight of the reactive dye. It is also apparent that the cost of a reactive dye must include the cost of the condensation reaction between dye and cyanuric chloride, which is over and above that required to produce the coloured part of the molecule. These two examples illustrate the likelihood that greater resistance to washing is attained only at some increased cost in synthesis of the dye and in the dyeing method.

This survey may be summarised as follows. Firstly, the history of research in dye making shows a very small number of chemical reactions unexpectedly yielding coloured molecules of great technical value. History also shows the value of close communication between dye-maker and user, as a result of which dyes of easier application and increased fastness have been synthesised.

Secondly, examination of all ranges of dyes on all the important fibres shows a wide coverage of colour gamut in dyes of high resistance to detergents. In general, there is no technical reason why the colours of textile goods should not be as permanent as are the materials themselves.

What then is the problem of the dyemaker? The increasing problem of the dyemaker is to decide whether the results of speculative research in the field of dyes and colour are likely to continue to be rewarding. Table VII shows the percentage

TABLE VII
Research Cost as a Percentage of Turnover

Name	Reference Year	Turnover × 10 ⁶	Research Cost × 10 ⁶	Research as % of Turnover
American Cyanamid	1956	\$500.7	\$22.4	4.5
Bayer	1956	DM1596	DM77	4.8
BASF	1956	DM1500	DM75	5.0
Ciba	1957	Sf891	Sf52.5	5.9
Du Pont	1956	\$1888.4	\$77.0	4.1
Hoechst	1957	DM1760	DM88	5.0

of gross turnover which the named dye and chemical manufacturers state are devoted to research.

The research work referred to in all these cases probably embraces three general categories. Firstly, work designed to improve the efficiency of manufacturing processes and to explore the possibility of alternative chemical routes. This clearly must go on until the dye manufacturer himself decides that his processes are so efficient that the return on more investigation is likely to be unrewarding. Secondly, research work is directed to improving the method of application of the products already manufactured; for example, this extends to the exploration of such new fields as those which arise when a new fibre becomes commercially available. This field too seems to have possibilities of a continuing reward. It spills over into the technologies of the consuming industries and relies greatly upon a close appreciation of their needs for it to be fully fruitful. Thirdly, research in the field of organic chemistry can be of a speculative nature, either embarked upon for some specific target, as was that of Böttiger when he set out to make an azo direct cotton dye, or of the less oriented and untargeted type which may lead at very infrequent intervals of time to a new organic chromophore.

For the purpose of the argument it can be assumed that the current world expenditure on dyes is of the order of £300 million. If we take 5% as an approximate figure for the percentage of turnover devoted to research, it is evident that £15 million in total may be spent each year on improving manufacturing processes, on improving methods of application, and on looking for new dyes and pigments. If one-quarter of the money spent is devoted to the speculative objective, then this is equivalent to £4 million, which in its turn means that about 1,000 chemists with an equal number of assistants are at this moment seeking

new dyes and new chromophores. Can the unsatisfied needs of the textile industry sustain such an army of speculative dye chemists?

The foregoing analysis is confined to a consideration of washing fastness with respect to shade range and ease of application, and in this case the question makes a qualified "no" the inevitable reply. Only a diminishing number of small and very specialised targets remain to be attacked, but were the analysis to be repeated in respect of light fastness, then it would be found that there are still areas of colour in a number of ranges of dyes with special applications which are not yet available with the high fastness to light that can be achieved in other colours. Unfortunately, high fastness to light cannot readily be forecast from chemical considerations of structure, except in a very general way. It will be necessary therefore to keep speculative research for textile dyes alive in the hope of achieving some "minor miracle" which will enable the range of high light-fast dyes to be extended.

The problem of the ultimate consumer who still encounters textile goods of poor washing fastness can broadly find alleviation, if not entire resolution, by using a selection from the 3,500 individual products of world dye manufacture.

IMPERIAL CHEMICAL INDUSTRIES LTD.

DYESTUFFS DIVISION

HEXAGON HOUSE

MANCHESTER 9

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EXTERNAL ADDRESS

Self-smoothing Cellulosic Fabrics*

J. T. MARSH

I—The original invention of crease-resisting textiles took place just before the formulation of the chemical constitution and molecular structure of cellulose, but subsequent developments have taken place side by side.

The conception of chain-molecules in varying degrees of lateral order is now generally accepted, but there are dangers of oversimplifying the picture of a network structure as solely comprising the crystallites and amorphous regions; insufficient attention is paid to the probable existence of a loose network having occasional junction points within the amorphous regions, as in the general theory of gel structures.

These junction points may be increased in number and variety to form a new network which is sufficiently entangled to impart properties of technical and commercial value.

In the technology of the various processes, the relative proportions of the different types of cellulose, their accessibility and reactivity, are all important and may be controlled to some extent; sensitivity to degradation and embrittlement are also influenced.

II—Of the large number of new effects which may be obtained by suitable entanglements of the molecular chains of cellulose, the most outstanding are associated with crease-recovery, both wet and dry.

These and other properties may be stabilised and made durable through the use of certain chemical compounds such as thermosetting resins (phenol-formaldehyde, urea-formaldehyde, or melamine-formaldehyde), reactant resins (bifunctional derivatives of imidazolidones and triazones), and linear reactants (formaldehyde, butanedioldiurethane, epoxy compounds, and glycols).

III—Self-smoothing fabrics of cotton and rayon require different amounts of reagent for a similar result, but the quantities are almost equal when calculated on the amorphous contents of the fibres.

There is some agreement between the anomalous behaviour of cotton and rayon on drying and on addition of the self-smoothing finish; in both cases the effects may be attributed to molecular entanglements, the disruption of which causes a return to the original properties.

With conventional chemical treatments the reticulation is accompanied by resin-formed bonds, heat-formed hydrogen bonds, and the usual hydrogen bonds; thus there is a network within a network, giving increased elastic recovery but also increased rigidity.

The mechanical properties of the treated fibres may be influenced by the amount of accessible cellulose and hence by the relative number of heat-formed hydrogen bonds; the latter may be broken after treatment by a form of caustic conditioning or mercerising, but they may be prevented from forming when the curing stage occurs in steam. Many of the characteristics of the final product may be due to the proportions of normal hydrogen bonds, heat-formed hydrogen bonds, and cellulose-resin-cellulose bonds.

Introduction

The invention of the crease-resisting process by Foulds, Marsh, and Wood in the laboratories of the Tootal Broadhurst Lee Co. Ltd.¹ took place when there was only a small pool of knowledge on which to draw.

In the Mather Lecture of the Textile Institute for 1957, it was stated²—

It is very difficult to imagine now the environment in which work was done on the crease-resisting process, even for those who were associated with the early research; the constitutions and molecular structures of cellulose and of wool keratin were unknown, the idea of the molecular chain was not postulated, colloids were very much of a mystery, and resins were nasty sticky messes fit only to be put down the sink because they did not crystallise like decent organic compounds.

It is now well known that the crease-resisting process went hand in hand with the development of rayon, and that it also gave an enormous impetus to the use of direct dyes, whose wet fastness was vastly improved by the treatment; the process also expanded at the same time as the development of what may be termed "fibre science". Altogether, the period from 1925 to 1939 may perhaps be regarded as the heyday of textile chemistry and physics³.

I—Cellulose

It is now generally accepted that cellulose consists of long molecular chains of glucose residues; in the fibres these chains arrange themselves

according to two types, which merge into one another through many intermediate variations. On the one hand, there is an organised lateral array of the molecular chains in parallel formation, known as the *crystallite*, and on the other hand, there is the completely random arrangement or amorphous chaos; it must be appreciated that there are many intermediate zones, for it is unwise to oversimplify the picture into discrete crystallites existing as islands in an amorphous sea.

Many of the individual molecular chains are sufficiently long to pass through more than one orderly region and more than one disorderly region; in this way the whole structure is held together.

Superimposed on the concept of crystalline order and amorphous chaos is a further arrangement, for the crystallites themselves may lie in parallel formation or in relative disorder. Parallel crystallites can be aligned in the direction of the long axis of the fibre, and this is termed *orientation*, but they may be *disoriented* or arranged at random. It is important to differentiate between amorphous cellulose and disoriented cellulose: the former refers to regions of molecular chains, and the latter to crystallites, in disorder.

One of the mysteries of cellulose is the fact that a molecular chain which is studded with hydroxyl groups should nevertheless be insoluble in water.

When cellulose is first formed, either in the native or in the regenerated state, it is laid down in presence of water, but as it dries a number of

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hydroxyl groups are freed from attachment to water and, if they are sufficiently close, become attached to one another by hydrogen bonds. In this manner there is an attachment between the chain molecules by virtue of hydrogen bonding between the hydroxyl groups of adjacent molecular chains and, where these lie in parallel formation, a micelle or crystallite is formed in which the greater number of the hydroxyl groups within the crystallite are inaccessible. Although the individual hydrogen bond may not be strong, a large number in close proximity obviously can be very powerful. Thus there are a sufficient number of hydrogen-bonded inaccessible hydroxyl groups to render cellulose insoluble in water.

This concept may be supported by the well known experiment with a filament of polyvinyl alcohol under tension; it is insoluble in water until the tension is released, when it dissolves, i.e. the inaccessible hydroxyl groups become accessible.

Within the crystallite of cellulose, the glucose residues in the chain are united by covalent bonds; the chain molecules in the plane of the glucose rings are separated by only 2.5 Å., so that it is reasonable to assume hydrogen bonding; but normal to the plane of the glucose rings the nearest distance between atomic centres is 3.1 Å., which is close to that expected for van der Waals forces. Hence there are three different types of bond holding the crystallite together.

With cellulose it is generally accepted that there are fringes of amorphous material at the ends of the micelles and that the hydroxyl groups in the fringes will be freed during the original drying; in the fringe, however, the chain molecules are only loosely bound because of the irregular disposition and number of the bonded hydroxyl groups. Thus on wetting and drying, the amorphous fringe opens and shuts like an automatic umbrella.

In connection with the moisture relations of cellulose, the well known phenomenon of hysteresis is due to the greater number of free hydroxyls available during desorption than during absorption. There is a making and breaking of cellulose-water bonds and of cellulose-cellulose bonds.

Reverting to the important fundamental principle of a number of molecular chains extending through more than one micelle and more than one amorphous region, this has given rise to the theory of a micellar network which holds the whole structure together; the proportions of crystalline and non-crystalline material are responsible for strength and flexibility.

It is often assumed that the knots in the network are the micelles themselves, and that the amorphous fringes act as hinges. This appears to be somewhat of an oversimplification. Native cellulose contains about 30% of amorphous material, and regenerated cellulose about 60%, or twice as much; as the molecular chains in these non-crystalline regions are neither straight nor parallel, it is statistically probable that they will meet or cross one another occasionally. In general, the situation of the molecular chains in the amorphous part of the fibre is left rather "in the air", which is a most

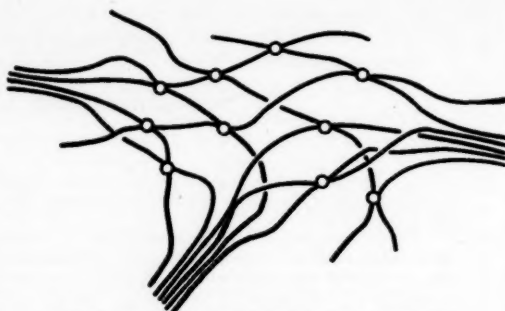


Fig. 1—Diagram of the Network Structure of Cellulose with Junction Points⁴

unlikely place for 30–60% of the fibre. There must be places where the chains come sufficiently close together to form some sort of entanglement by hydrogen bonds at "junction points" (Fig. 1⁴).

The concept of junction points forming a lattice in the structure of all gels was formulated generally by Frey-Wyssling⁵ in prewar days, but goes back even to von Nägeli⁶ in 1879.

The cellulose network with its various junction points, like press-studs, lies within the amorphous regions of the fibre, the swelling value of which is largely determined by the geometrical structure of the micellar system and the extent to which the amorphous network can expand without excessive strain. With regenerated cellulose, for example, the primary gel has 100% greater swelling in water than after the first drying and rewetting; this is due to the formation of new junction points which are immune to water. The network is compressed as it shrinks, so that new junction points are formed where the molecular chains approach one another sufficiently closely and in suitable positions; the process of involution prevents the formation of a monocrystal.

During the collapse of a fibre from the highly swollen gel it is necessary only for a very few junction points to form to account for the difference in swelling between dried and never-dried fibres; the small number of these junction points is evidenced by the fact that swelling power may be reduced without much alteration in the absorption of water vapour, or in other words, without much alteration in the amount of amorphous cellulose. The process of collapse, and the folding of the strings of the net, presupposes the displacement of the free chains, which become more constrained as the number of junction points increases; where there are sufficient of these in close proximity, the degree of swelling on rewetting will be reduced.

The conception of the network being contained within the amorphous regions of cellulose by a system of junction points (Fig. 1) owes much to Hermans and the Dutch school⁴, and deserves more appreciation than it appears to receive.

The existence of junction points in the amorphous parts of the fibre is demonstrated by the effect of moisture on the load-extension relations: the randomly formed hydrogen bonds are broken as the amorphous regions are extended and the chains uncoil. It is in agreement with the recovery of isotropic filaments and also with the recovery of

TABLE I
Water-retention of Mercerised Cotton¹²

Treatment	Without Tension		With Tension	
	Water retained (%)	Treated Untreated	Water retained (%)	Treated Untreated
Mercerised and washed at 15°C.	87.8	5.35	50.3	3.06
Mercerised and washed at 60°C.	73.4	4.48	42.6	2.60
Mercerised and washed at 100°C.	60.6	3.69	42.2	2.57
Mercerised, washed, and dried at 15°C., then rewetted	56.5	3.44	33.9	2.06
Mercerised and washed at 15°C., dried at 100°C., and rewetted	49.9	3.04	28.2	1.72

rayon which has been highly stretched in the wet state, for even the well oriented fibres have some free chains, more or less contracted, in the amorphous portions, and where the chains cross one another there will be a tendency to form junction points with a consequent reduction in the free length of the chain molecule.

The mechanism of rheological behaviour due to hydrogen bonding in general has been reviewed by Nissan⁷.

Most cellulose chemists would probably agree that for many years too much attention has been paid to the crystalline portion of the fibre and not enough to the amorphous regions; it should be remembered that crystallisation is only one aspect of hydrogen bond formation in cellulose. It is also important to consider both the micellar network and the amorphous network.

DISPERSED CELLULOSE

In the earlier researches which led to the crease-resisting process, it was the intention to form a synthetic resin within the fibre itself, and great attention was paid to the possibilities of a swollen fibre as a means to that end⁸; hence there was considerable interest in the mercerising phenomenon⁹.

During the mercerising process there is a great lateral swelling of the fibre, but the accompanying shrinkage in length is generally prevented in works treatment; although the best results are obtained with shrinkage followed by stretching, this is not universal practice. The highest degree of swelling is obtained under conditions of free shrinkage.

The great opening of the whole structure which occurs as a result of mercerising is accompanied by a very large increase in the number of free hydroxyl groups which become available for combining with water and with dyes; the fibre becomes more absorbent, as is well known. With the increased number of free hydroxyl groups there will be an increased freedom of movement of the chain molecules in the amorphous regions of the fibre.

Quantitatively, the available hydroxyl groups of mercerised cotton lie between those of native cellulose and regenerated cellulose, where the

structure has been completely disintegrated and re-formed; the ratios for native, mercerised, and regenerated cellulose are roughly 1:1.6:2.0.

Mercerisation increases the amount of amorphous material in the fibre, for both the size and the proportion of the crystallites are decreased.

As early as 1908 Knecht¹⁰ found, by measuring the absorption of dyes, that the accessibility of mercerised cotton is affected by the conditions of drying.

During the course of their work on the absorption of sodium hydroxide solutions by cotton, Coward and Spencer¹¹ measured the water retained after removal of the alkali; the method was to centrifuge at about 3,000 *g* for 2.5 min. They obtained good correspondence with the conclusions of Knecht, but also made the important observation that the water-retention of never-dried mercerised cotton could be reduced from 108% to 88% by boiling in water for 6 hr.

The effect of the temperature of washing and of drying on mercerised cotton was further examined by the writer¹², who utilised a centrifuge with an acceleration of about 6,500 *g* (cf. Table I).

For many years the effect of drying has been recognised by the practical dyer in a qualitative manner, and there has been much warning as to the dangers of "overdrying". It is also well known that drying at a high temperature, and under tension, particularly with rayon, can give harsh or stiff effects with an otherwise soft fabric.

Some quantitative work of Weltzien¹³ has conveniently been summarised by Rümens¹⁴ (Table II).

In addition there are the other methods of estimating the accessibility of cellulose, such as iodine, sodium hydroxide, and baryta absorption, absorption of copper from cuprammonium, and the absorption of water vapour to which reference has recently been made by Urquhart¹⁵.

The maximum increase in absorptive capacity occurs under conditions of minimum tension, and for this reason alone the interpretation of absorption ratios as a measure of mercerising efficiency needs care; furthermore, absorptive capacity may be reduced by the temperatures of washing and of drying, and of other subsequent treatments. It is

TABLE II
Swelling after Repeated Drying at 105°C.¹⁴

No. of dryings	0	1	2	3	4	8	Decrease (%)
Cotton	55.8	44.7	42.0	40.4	39.6	—	29
Viscose rayon	124.9	116.0	109.5	103.5	97.1	80.2	35

a measurement which includes amorphous cellulose and accessible hydroxyl groups without distinguishing between them. Whereas it is possible to achieve an absorption ratio of 1.6 in mercerised cotton, most mercerised fabrics only reach a figure of 1.25.

However, it is possible to measure the reactivity ratio of mercerised cotton¹⁶, which varies according to the tension applied during mercerisation but is not appreciably affected by boiling water or by dry or wet conditions of heating. Accordingly, it is a more reliable index of the amount of amorphous cellulose in the fibre.

It should not be forgotten that amorphous cellulose may contain inaccessible hydroxyl groups, and that the crystallite will contain accessible hydroxyl groups, particularly on the surface.

The formation of a few hydrogen bonds by heat can reduce the free length of some molecular chains in the amorphous region and so restrict swelling and water-imbibition, without having any appreciable influence on the absorption of water vapour.

From the above comments it will be seen that sometimes there is a danger of confusing amorphous cellulose with accessible cellulose: they are not identical. Similarly, there is occasional lack of differentiation between accessibility and reactivity.

Perhaps a finer point of distinction to which attention may be drawn is that which lies between reactivity and sensitivity, and which is not always appreciated. *Reactivity* properly refers to rate of reaction; thus regenerated cellulose is more reactive than native cellulose. However, because native cellulose contains crystallites which are actually much larger than those of regenerated cellulose, and also contains a lower percentage of

amorphous material in the fibre, it only requires the cleavage of a few free molecular chains in the amorphous network with its junction points to produce much greater relative damage than on rayon with its greater number of free chains and more extensive network.

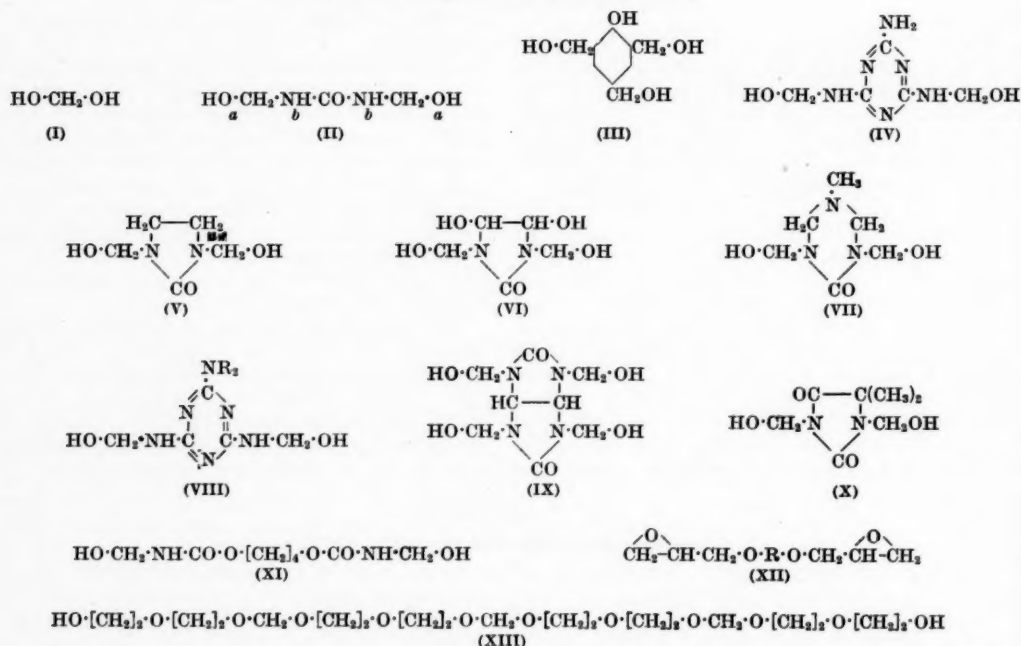
In many reactions, cotton is more sensitive than rayon; for example, it is not possible to treat cotton with acidified formaldehyde to form cellulose methylene ether and produce anti-shrink fabrics which are sufficiently strong for merchandising, but this can be done with rayon. Furthermore, it is possible to degrade cotton by acid hydrolysis until it has no measurable tensile strength, but the product will nevertheless form a regenerated cellulose of normal strength. Hence, although rayon is mechanically weaker than cotton, and although it is more reactive, it is nevertheless frequently less sensitive to chemical attack.

Sensitivity appears to depend on the distance between the crystallites; this conception has been subjected to mathematical analysis by Sippel¹⁷ and extended by Conrad and his colleagues¹⁸, thus explaining the relatively large fall in strength of untreated cotton compared with mercerised cotton or rayon at similar percentages of broken molecular chains.

II—Chemical Reagents

It is not proposed to discuss the crease-resisting results obtained in 1929 by Battye and Marsh¹⁹ with borates, silicates, and stannates, which probably depend for their effect on entanglements by complex-formation, but rather to restrict the field to the more interesting chemical compounds which seem to act in virtue of two or more

TABLE III
Chemical Reagents for Crease-recovery



functional groups, generally the hydroxymethyl or "methylol" group $-\text{CH}_2\text{OH}$.

Many of these compounds have received attention from various authors^{14, 19, 20}. The formulae of thirteen of the more important compounds are set out in Table III so as to demonstrate certain common features.

ADVANTAGES OF RESIN TREATMENTS

Although the property imparted is often called crease-recovery, it is accompanied by many other outstanding improvements, and no really satisfactory single word has been found to embrace them all. Some of the effects obtained are listed below—

- Improved resistance to and recovery from creasing
- Smooth-drying properties after laundering
- Durable effects may be imparted by intermediate mechanical treatment
- Reduced laundry shrinkage
- Increased dry tensile strength and greatly increased wet tensile strength of rayon
- Improved fastness to washing and rubbing of most dyes
- Decreased water-imbibition and more rapid drying
- Improved handle and drape of fabrics
- Increased weight
- Increased resistance to distortion of fabrics with improved retention of garment shape and freshness
- Improved resistance to slippage and fraying
- Vehicle for modern flameproofing agents
- Increased resistance to photodegradation and weathering
- Increased resistance to rotting.

Although it is not intended to discuss the craft of textile finishing, but rather to confine the subject-matter of the present paper to textile chemistry, yet three finishing developments should be mentioned, as additions to the original crease-resisting property, with concomitant additional advantages.

First there are durable mechanical effects, such as the Everglaze embossed and glazed finishes, stiff finishes, and durable pleating. These depend on mechanical treatment of the resin-impregnated cloth before it has been hardened; their development owes much to the work of the Joseph Bancroft & Sons Co., of Wilmington, U.S.A., in co-operation with the Calico Printers Association of England, and Raduner of Switzerland.

Secondly, there is the more recent smooth-drying finish, the possibility of which dates back to 1944, but which has been developed along with a similar property in synthetic fibres since 1954. The smooth-drying fabric is not an inevitable consequence of resin-treatment, but is intended to meet a somewhat complicated set of final requirements; it is here that a strict measure of quantitative control, such as that provided by the Smooth-drying Index (TBL), is a great asset to the cognoscente.

Thirdly, resin-treatment seems to form the basis of a number of durable flameproofing treatments, such as urea phosphate, THPC (tetrakis(hydroxymethyl)phosphonium chloride), BAP (brominated allyl phosphonitrilate), and APO (tris-1-aziridinylphosphine oxide), used in conjunction with or as part of the resinous precondensate.

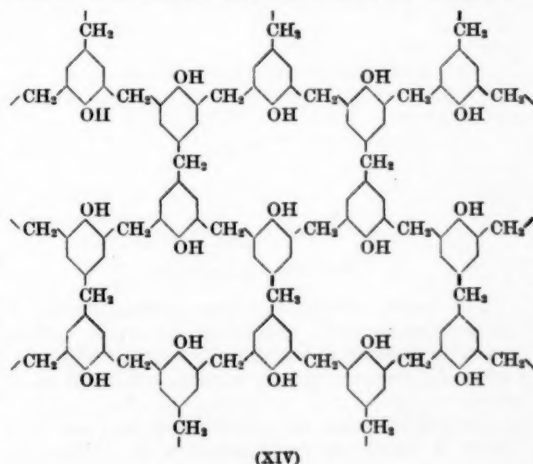
FORMALDEHYDE

Formaldehyde in presence of an acid catalyst is the oldest, cheapest, and most destructive reagent for obtaining crease-resisting effects on cotton and rayon; the apparently simple reaction is complicated by the competition between combination and evaporation on the one hand, and between combination and acid hydrolysis on the other hand. Formaldehyde behaves as a bifunctional reagent, i.e. as methylene glycol (I, Table III); there is strong probability, but no proof, that it forms covalent cross-linkages with cellulose, and this idea has given a great bias to all later considerations of the mechanism of crease-resistance. There are several anomalies concerning cellulose methylene ether, and one of the most interesting is the greater devastation of cotton compared with rayon, even allowing for the hypersensitivity of the stronger fibre with its smaller region of low lateral order.

When formaldehyde is combined with highly swollen cellulose, there appears to be cross-linking with diaeresis, giving "wet but not dry" recovery, as opposed to the more usual dry recovery produced by syneresis; hence water-imbibition is not a satisfactory index of cross-linkage. "Wet but not dry" recovery may be produced also by reaction with other cross-linking reagents such as dichloropropanol²¹. The subject has been examined by the writer^{22, 23}.

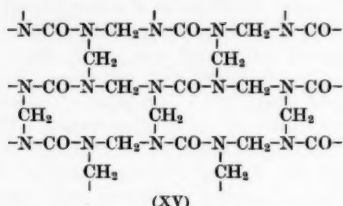
THERMOSETTING RESINS

The first commercial crease-resisting cellulosic fabrics were prepared by treatment with phenol-formaldehyde, the criterion of success being to synthesise the resin within the fibre. The simple condensation product (III) has three reactive methylol groups and condenses under alkaline conditions to form a three-dimensional network (XIV).



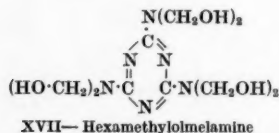
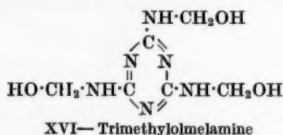
Phenol-formaldehyde is only of historic interest now, on account of its intense discoloration, but its effect as a "crease-proofer" should not be forgotten by those who strongly uphold the theory of covalent cross-linkages with cellulose as the explanation of the crease-recovery effect.

Urea-formaldehyde was the second resinous condensation product to be used for crease-resisting and it still remains the most popular. Dimethylol-urea (II) is only bifunctional in respect of methylol groups (a), but it contains also two reactive secondary amino groups (b), so that it, too, may form a three-dimensional network (XV). The structure is idealised, for there are many gaps and voids in the lattice, leaving reactive nitrogen sites, such as secondary amino groups.



The formation of tri- and tetra-methylolureas has been postulated, but their existence has not been proved to the satisfaction of older and more critical schools of organic chemistry. An interesting suggestion that the early stages of condensation may be through triazines or similar ring structures was made by Marvel²⁴, but in the series of papers by Zigeuner²⁵ this is discounted. The chemistry of the aminoplasts continues to be actively investigated, and a useful review of recent work has been made by Glauert²⁶.

The third thermosetting resin to be used was melamine-formaldehyde. Melamine, 2,4,6-triamino-1,3,5-triazine, readily forms methylol derivatives with formaldehyde, e.g. dimethylolmelamine (IV, Table III); actually trimethylolmelamine (XVI) is more commonly used for crease-resisting work. Unlike urea, all the amino hydrogens are replaceable, so that it is possible to form hexamethylolmelamine (XVII).



The resin, which, like urea-formaldehyde, is formed under acid conditions, is much harder, possibly because of a tighter network, and is also more difficult to hydrolyse with either alkali or acid.

As melamine has an amino group to spare, as it were, it offers various possibilities in addition to

crease-resistance: the "spare" amino group may be used to attach a fatty chain for softening or water-repellency, to attach appropriate atoms or groups for flameproofing, and also to impart various other properties. There is little doubt that still more will be heard of this polyfunctional compound in the future.

Another variation on the main methylol products of both urea and melamine is the methyl ether, which has improved stability both to ageing and in the impregnating bath.

REACTANT RESINS

Melamine is more expensive than urea and does not lend itself to the "do-it-yourself" methods of making precondensates; accordingly, certain arguments were advanced in its favour, such as obviating the use of a catalyst, greater resistance to hydrolysis, and a low affinity for chlorine from hypochlorite. The last point seemed to make a popular appeal in a country which is averse to the use of hypochlorites for commercial bleaching, and it was soon found that the real issue was not one of chlorine absorption but of the damage caused when hydrochloric acid is liberated on subsequent heating; furthermore, there is some discoloration when melamine-formaldehyde is chlorinated. The importunities of hypochlorite-happy housewives in the U.S.A. were the cause of a search for reagents which would give crease-recovery without chlorine-retention damage, or discoloration.

One of the first to be applied was cyclic dimethylol-ethyleneurea or -2-imidazolidone (D.M.E.U.) (V); it is only bifunctional and does not form a thermosetting resin. As it tends to combine with cellulose rather than with itself, it is called a *reactant* resin. During the past five years it has become very popular, and in 1957 accounted for 30% of the resins used in the textile industry.

A somewhat similar product, dihydroxy-dimethylol-ethyleneurea (VI) is used in Germany and other countries as Fixapret CP (BASF). It is of interest to the chemist as coming from glyoxal, urea, and formaldehyde, which may also be used to make tetramethylolacetylenediurea (IX) as well as dimethyldimethylolhydantoin (X); the last two compounds have been used in Europe to a limited extent.

The dimethylol-ethyleneureas have found their greatest outlet on cotton goods, mainly white goods, and about 1,000 million yards of cotton was treated in 1957 in the U.S.A.; this is approx. 20% of wearing apparel for that country. From formula V it will be seen that there should be no nitrogen sites available for chlorine, but in actual fact there is a slight absorption of chlorine because the D.M.E.U. is not pure; moreover, it is rather susceptible to acid hydrolysis, after which there is a greater tendency to chlorine-retention damage.

One of the first attempts to deal with the modest amount of hydrochloric acid which may arise from chlorination of goods treated with D.M.E.U. was to employ a metallic salt, such as magnesium chloride or zinc nitrate, as catalyst in the reaction of D.M.E.U. with cellulose; after neutralisation and washing, the metallic oxides present in the treated

fabric were expected to fix any hydrochloric acid which might come from the action of hypochlorite on the treated goods followed by heating, and to reduce the discoloration with melamine.

A second method of dealing with the problem was to use, with D.M.E.U., a compound which was more basic, e.g. melamine, and which would therefore possess greater buffering powers. There are various patents²⁷ for the use of such mixtures in specific proportions.

The most recent method is to use suitable reactive compounds which contain in themselves a suitable buffering system; these are triazones (VII), and although the methyltriazone is shown in the formula, it seems that the ethyltriazone is more commonly utilised. They are manufactured quite simply by reaction of dimethylolurea with the appropriate amine; unfortunately, many of these compounds are impure and give rise to unpleasant odours. Although the resistance of the triazones to hydrolysis is better than that of the cyclic ethyleneurea derivatives, nevertheless it is not outstanding. The chief interest to the chemist resides in the buffering mechanism of the tertiary nitrogen, for the buffering power is renewed every time the fabric is washed in soap or alkali.

It is also possible to increase the buffering power of melamine, as in formula VIII, and to block the nitrogen sites, but such compounds are expensive, even if highly efficient.

Chlorine-retention damage has been mentioned only as a factor which has renewed the interest of the chemist in the process and has influenced the search for new products (although some of them are actually old in the chemical literature); the subject of chlorine retention has been fully discussed in the important publications of Nuessle and Bernard²⁸ and of Nuessle²⁹.

LINEAR REACTANTS

The simplest of the linear reactants, as distinct from the cyclic products, is formaldehyde, which has already been discussed. Attempts by Gagliardi and Nuessle³⁰ to provide a longer cross-linkage, and so reduce embrittlement, were generally accompanied by poor crease-recovery.

Dimethylolbutanedioldiurethane (XI) is believed to be the basis of Fixapret BU (BASF), which is distinctly unusual in giving better crease-recovery with rayon than with cotton; both resistance to abrasion and resistance to washing of the treated products are good, according to Rümens³¹.

Two recent products have been made on a non-nitrogenous basis and are therefore free from chlorine retention, but there is little information about their use on a works scale. The epoxy compounds (XII) are somewhat expensive at the moment, and a good recovery from creasing is accompanied by rather large losses in strength. Some of the acetals (XIII) are useful for anti-shrink effects, but the chief product of this type to give good crease-recovery is that obtained from pentaerythritol $C(CH_2OH)_4$; the loss in strength of cotton is substantial, and there is also an acrid odour of acetaldehyde during the final condensation. At the moment, however, it is too soon to

adjudicate on the merits of the non-nitrogenous linear reactants or even to decide whether the strength losses are due to chemical combination or acid hydrolysis of the cellulose.

EFFICIENCY

Many of the compounds previously mentioned have been discussed on a basis of efficiency; for example, it has often been stated that D.M.E.U. is more efficient than other reagents because it gives a higher degree of recovery from creasing for a given weight, but it also seems to impart a higher degree of embrittlement to cotton.

The relation between embrittlement and recovery has been examined on several occasions, but perhaps the most detailed set of results is due to Smith³², who established the same linear relation between recovery and strength losses for three different amino-aldehyde resins (Fig. 2); this important generalisation points to the difficulty of obtaining good strength with good recovery, particularly as some products may give increased damage with the high recovery needed for the smooth-drying effects. It seems that chemistry is not enough.

Another important outcome of the comparison of various products—such as dimethylolurea,

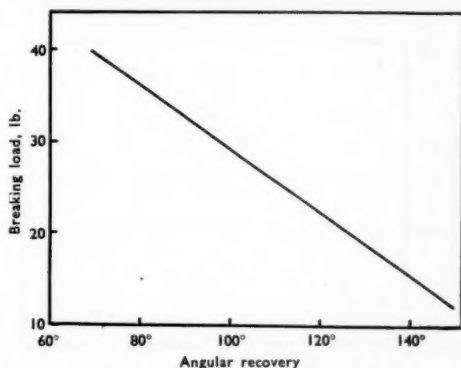


FIG. 2—Relation between Breaking Load of Crease-resisting Cotton and the Angular Recovery³²

trimethylolmelamine, and dimethylolethyleneurea—on the basis of recovery and the amount of resin is the demonstration by Cooke and his colleagues³³ that the relation between recovery and molecular concentration of the three products is essentially a single curve (cf. Fig. 3 and 4).

An interesting survey of the quality of crease-resisted fabrics was made by Best-Gordon³⁴.

At the present time, the four main products employed for the production of the self-smoothing finish are—

- Dimethylolurea (D.M.U.)
- Dimethylolethyleneurea (D.M.E.U.)
- Dimethyloltriazone (D.M.T.)
- Methylolmelamine (M.M.M.).

Often the deciding factor is chlorine-retention, which has been discussed by Schefer³⁵. There are few comparisons of the relative efficiencies of the products, but Table IV may be of general interest, as it relates to the results obtained by

TABLE IV
Comparison of Four Resin Finishes³⁶

	Rip (g.)		Flex Abrasion (cycles)		Breaking Strength (lb.)		Crease-recovery (°)		Chlorine Damage (% loss in strength)
	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft	
Untreated	1140	827	1625	1130	44	36	95	89	1
4-3% D.M.U.	500	253	80	110	30	18	143	136	64
3-7% D.M.E.U.	540	333	115	75	28	22	147	148	6
4-3% D.M.T.	640	413	180	90	27	19	151	147	9
4-8% M.M.M.	607	347	140	90	31	22	143	139	5

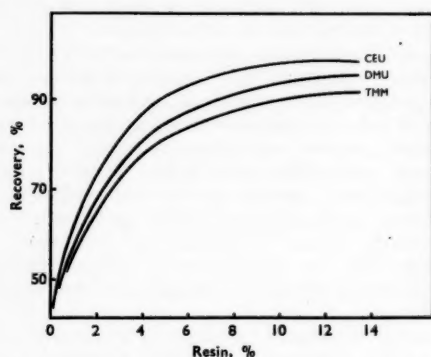


FIG. 3—Comparison of Dimethylethyleneurea, Dimethylolurea, and Trimethylolmelamine as Crease-proofing Agents for Cotton³³

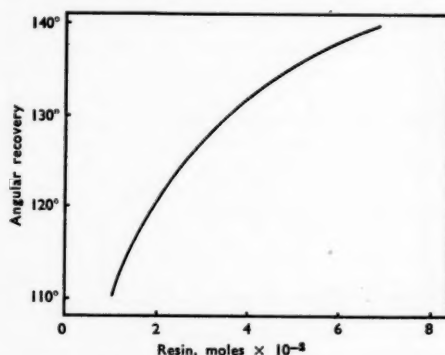


FIG. 4—Relation between Crease-recovery and Molecular Concentration of Dimethylethyleneurea, Dimethylolurea, and Trimethylolmelamine³³

Reid and his colleagues³⁶ on the popular 80 × 80 cotton print cloth. However, the many variables and the different objectives render any comparisons of rather limited value.

III—Self-smoothing Fabrics

In the conventional crease-resisting process, invented by Foulds, Marsh, and Wood¹, the criterion of success is to form the resin inside the fibre; there have been no fundamental changes in the process for thirty years, but the application has extended enormously³⁷.

Self-smoothing fabrics are the latest development in finishing technique, and the term is intended to include wet and dry crease-recovery, wash-and-wear, minimum-iron, and many other features of considerable textile value.

There are certain differences between treated cottons and treated rayons, however, to which

particular attention may be drawn in connection with theoretical considerations. Firstly, the usual quantity of added resin in rayon is twice that in cotton (Fig. 5), and this corresponds with the proportions of amorphous material in the fibre; hence the amount of added resin is the same when calculated on the amorphous cellulose. Secondly, the extension at break of treated cotton and rayon is lower than with the original material, but the

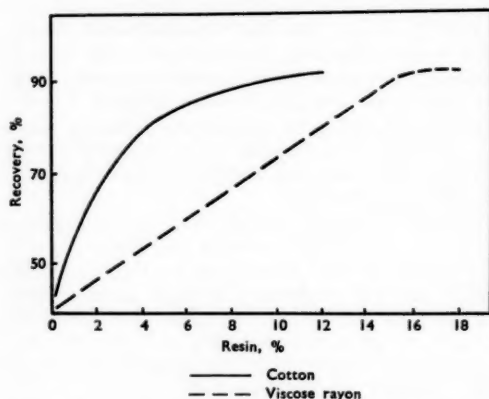


FIG. 5—Relation between Crease-recovery and Added Resin for Cotton and for Viscose Rayon

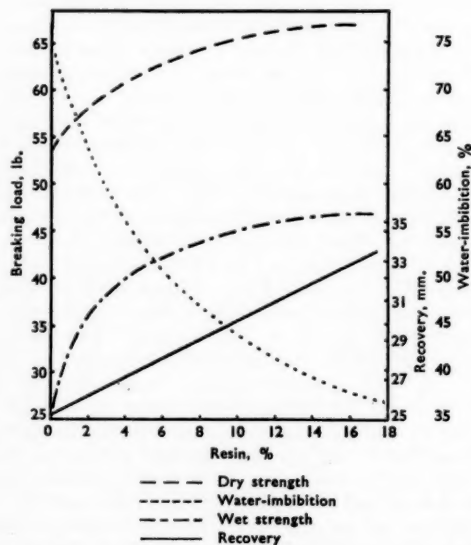


FIG. 6—Effect of Added Resin on the Physical Properties of Viscose Rayon

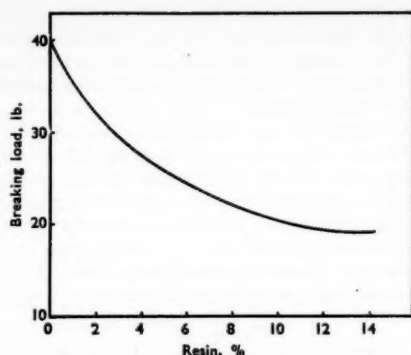


FIG. 7—Breaking Load of Crease-resisting Cotton as affected by Added Resin

tensile strength of rayon is improved by the process (Fig. 6), whilst that of cotton is reduced (Fig. 7); the physical properties of the fibres are restored when the resin is removed³⁸, indicating that the reduction in extensibility is due to reversible physical embrittlement and not to irreversible chemical degradation.

The resistance to creasing imparted by the presence of the resin was attributed to molecular entanglement as long ago as 1937³⁹, the exact nature of the bond between the resin and the fibre being a secondary matter.

It is part of the folklore of the crease-resisting process that completely dried cotton exhibits a high degree of uncreasing when subjected to the clenched-fist test, but that the property is soon destroyed as the cotton absorbs moisture. The first observation of this phenomenon is not known with any certainty, but it was definitely noted by Barrett and Wood independently in the period about 1919. It has been mentioned subsequently^{39, 40} with the suggestion that the effect—

... is probably due to the crumpled and disorientated molecular chains coming close together as the water is removed, so that the cohesive forces are at a maximum; as drying proceeds, the molecular chains approach and the hydroxyl groups undergo mutual attraction, possibly with hydrogen bonding, and set up a molecular entanglement of the crumpled chain molecules.

This hypothesis is now supported by the views of Hermans and others on the amorphous network with its junction points.

The effect of moisture regain on the crease-recovery of various fibres later discussed by Elöd and Etzkorn⁴¹ shows the interdependence of the two properties (Table V), but was not taken to its logical conclusion; nevertheless, extrapolation to dryness confirms the old observation.

TABLE V
Recovery (%) and Humidity⁴¹

R.H. (%)	Viscose Rayon	Cellulose Acetate	Silk
92	17	22	23
65	32	48	78
30	54	58	95

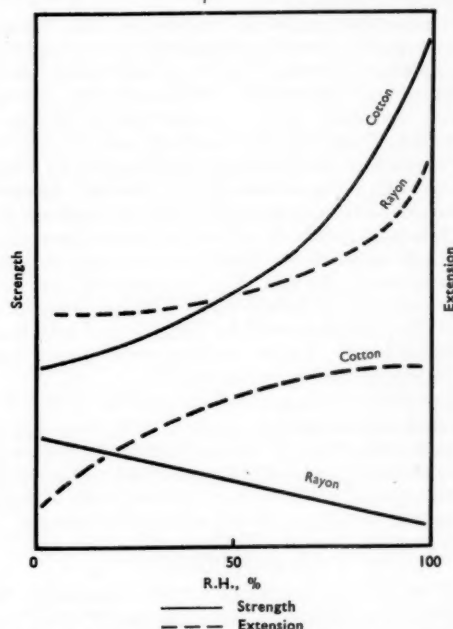


FIG. 8—Effect of Humidity on the Strength and Extension of Cotton and Viscose Rayon

Still more interesting, perhaps, are the changes in physical properties of cotton and rayon which accompany the absorption and desorption of moisture; some of these have been collected by the writer⁴², and are now given in a graph (Fig. 8) for convenience. It is well known that with both cotton and rayon the extension at break increases with increase in moisture content, but, whilst the tensile strength of cotton increases, that of rayon diminishes; it is not sufficiently appreciated that with decrease in moisture content the extensibility of cotton and rayon diminishes, but the strength of the former falls whilst that of the latter rises. Hence there is close agreement between the effects of drying on crease-recovery, strength, and extensibility, and the effect of internal resin formation on the same properties (see Table VI); both may be attributed to molecular entanglement—unstable or stable—the disruption of which causes the return of the original properties in both cases.

Crease-recovery by resin formation, however, is not believed to be due to a form of permanent

TABLE VI
Crease-resisting Products

Treatment	Cotton		Rayon	
	Strength	Extension	Strength	Extension
Physical—drying	Loss	Loss	Gain	Loss
Chemical—formaldehyde	Loss	Loss	Gain	Loss
Physicochemical—resin	Loss	Loss	Gain	Loss

dehydration, for when the moisture content of resin-treated cellulose is estimated on the cellulose rather than on the cellulose plus resin, it follows the normal course, as shown by the writer⁴³ and confirmed by Landells⁴⁴; furthermore, the recovery from creasing of the treated fibres varies with relative humidity and follows the normal curve for moisture absorption⁴⁵.

The conventional crease-resisting processes, however, include a final condensation of the resin at temperatures of around 140°C. or even higher, under substantially anhydrous conditions. It is suggested, therefore, that a considerable amount of reticulation takes place, which depends mainly on the formation of very strong junction points, where the synthetic resin acts as the bonding medium between the molecular chains; this is supplemented by junction points of hydrogen bonds formed at the high temperature, which are probably stronger than normal. In this way, the network system is stabilised by cellulose-resin-cellulose bonds at intervals, supplemented by heat-formed cellulose-cellulose bonds; it also contains some of the usual hydrogen-bonded junction points.

The thermosetting resins themselves form three-dimensional networks, so that there is a highly complicated structure of a resin network within an amorphous network within a network of molecular chains and crystallites; it is not surprising that the treated material exhibits good crease-recovery.

PREMERCEERISATION

From the very beginning of the research into the application of resins to textiles it was believed that the criterion of success was to form the resin within the fibre, so that on somewhat empirical grounds it was considered that an absorbent fibre with a tendency to swell would be better starting material than a non-absorbent or collapsed fibre; hence the interest in mercerisation, which was encouraged by the writer's observation in the autumn of 1927 that rayon was strengthened by resin treatment although cotton was weakened. The fundamental reasoning was wrong, but the time had not yet arrived for the publication of the work of Meyer and Mark (1928)⁴⁶, which led to considerations of unit cells, micelles, crystallites, and other aspects of the modern conception of the structure of fibres.

In USP 1,734,516¹ it is clearly stated, however, that the cotton should be treated with a swelling agent before impregnation with the resinous condensation product; not only was mercerisation recommended, but it was advised that this preliminary process must be well done. Further considerations about swollen fibres led to work on never-dried mercerised cotton⁴⁷; this gave useful

improvements by methods which were regarded as somewhat inconvenient on the works scale of production, owing to the tedious exchange of water for impregnating solution and the difficulties of constant concentration.

Under normal conditions of processing, both unmercerised and mercerised cotton suffer a fall in breaking load (Table VII) which varies in extent according to the nature of the crease-resisting treatment; the breaking load is also affected by other factors, such as tension, during impregnation, drying, and heating. There is generally a greater effect on the weft or filling of the fabric than on the warp.

TABLE VII
Ripping Strength (g.) of Cotton

	Unmercerised	Mercerised
Untreated	550	900
Treated	220	500

Characteristic figures compiled over a number of years indicate an average of about 15% reduction in breaking load, and this is more closely associated with the improvement in crease-recovery than with the amount of resin in the fibre. With unmercerised cotton, however, the fall in breaking load is greater than with mercerised cotton and averages about 25%. Reduction in extension at break and in tearing strength also indicates embrittlement of the fibre as a result of the resin treatment; there are many data in the literature.

The difference in result between resin treatments of mercerised and unmercerised cottons has been confirmed by American work⁴⁸, in which both urea-formaldehyde (10-12%) and melamine-formaldehyde (6-7%) were employed. Treated unmercerised cotton gave a breaking load of 26 lb., or 40% fall in strength, whilst treated mercerised cotton gave a breaking load of 34 lb. (23% fall).

The effect of mercerising has also been investigated by Smith³², who employed 10% of methoxymethylurea on a plain-weave cotton fabric; improvements in tensile and ripping strengths (over those of resin-treated unmercerised cotton) were confirmed (Table VIII). The actual data show little benefit in respect of recovery from creasing; the mercerised fabric, however, loses only 24% of its tensile strength compared with a loss of 47% with the unmercerised cloth, whilst the loss in ripping strength of the mercerised cotton is 52% compared with 63% for the unmercerised cotton. The differences are quite pronounced, although the actual losses appear to be rather great.

Many textile chemists, including the writer, are of the opinion that breaking load is a rather unsatisfactory index of quality; for example, a high

TABLE VIII
Effect of Premercerisation on Strength of Cotton³²

	Recovery (%)	Tensile (lb.)	Loss in Tensile Strength (%)	Rip (g.)	Loss in Rip Strength (%)
Unmercerised, untreated	52	66.2	47	124	63
Unmercerised, treated	86	34.7		46	
Mercerised, untreated	57	65	24	145	52
Mercerised, treated	84	50		69	

breaking load may accompany inextensibility. Crease-resisting cotton, prepared under tension, may have a breaking load in excess of that of the untreated material, but there is a severe fall in extension at break, ripping strength, and resistance to abrasion. Unfortunately, measurements of extension are more difficult to make than those of breaking load (with cotton at all events), and there is no agreement on methods of testing ripping strength or resistance to abrasion. Although ripping strength is closely related to fibre strength, it can be influenced by friction; hence the great interest in the use of softeners, so that the stress is more uniformly distributed.

Rümens¹⁴ has provided a host of data confirming the superiority of treated mercerised cotton over treated unmercerised cotton in respect of tearing strength and extension at break.

The superior physical properties obtained with mercerised cotton are mainly due to the fact that mercerisation increases the amount of amorphous cellulose in the native fibre; not only is the original amount relatively small (30%), but cotton contains large crystallites. Hence it requires the immobilisation of only a few of the free chains by resin-cellulose bonds to give a substantial increase in rigidity and to cause embrittlement by a loss of flexibility.

Mercerised cotton contains more amorphous cellulose with a greater number of free chain molecules, probably of greater free length, so that the resin-cellulose bonds do not exert such a great effect on the rigidity of the fibre.

Furthermore, in addition to the resin-cellulose bonds there will be a number of cellulose-cellulose bonds exerting an effect which is stronger than normal because of the temperature of the final condensation of the resin; these cellulose-cellulose bonds will supplement the effect of the resin-cellulose bonds to a greater extent in those regions of amorphous cellulose which are small, for they will tend to act in the fringe of the micelles as well as in the more remote parts of the non-crystalline cellulose.

POSTMERCEMERISATION

The aftermercerisation process for crease-resisting fabrics arose directly from a serious defect of treated linen, which normally suffers such a degree of embrittlement as to render the goods unmerchantable.

Crease-resistant linen was first aftermercerised by the writer in the spring of 1933, in an attempt to make the treated fabric softer and more supple; mercerisation was carried out under tension, and there were different opinions as to the degree of improvement. Later, and much more successful work was carried out independently by Corteen, Foulds, and Wood, who performed the aftermercerisation without tension and obtained such striking improvements that the whole character of crease-resistant linen was transformed, particularly when the original fabric was constructed with a view to permitting the necessary amount of shrinkage in the final stages. There can be little doubt that without this treatment there would be

no crease-resisting linen, nor indeed would there be any smooth-drying linen.

According to the patented process⁴⁹ a typical method of procedure is to start with a bleached mercerised linen fabric 36-38 in. wide, and to impregnate this with an amino-aldehyde precondensate in the usual manner. An excessive amount of resin must be avoided, since this would prevent the shrinkage in both warp and weft directions required during subsequent treatment without tension in sodium hydroxide solution for several minutes. The fabric is finally finished at about 34-36 in. wide.

The swelling process imparts a great improvement in strength and durability, the resistance to abrasion showing a manifold increase. The breaking load on the same number of weft threads also shows a great increase (Table IX).

TABLE IX
Breaking Load of Linen

Treatment	Breaking Load (lb.)
Crease-resist only	17.3
Treated and postmercerised	>30

This invention is all the more remarkable in that the water-imbibition of the treated and mercerised linen is greater than the figure for the untreated linen (Table X).

TABLE X
Water-imbibition (%) of Linen

Treatment	Fabric A	Fabric B
Untreated	63.5	54.5
Treated and postmercerised	69.6	62.0

Not only is the creasing of untreated linen notorious, but the mercerisation treatment is very difficult; furthermore, when untreated linen is mercerised without tension there is a fall in tensile strength of about 8%⁵⁰. Altogether, the postmercerisation of linen is quite remarkable.

Substantial improvements can also be made by the aftermercerisation of treated cotton, but these are less striking.

The effect of the mercerisation of crease-resisting cotton has been confirmed by Mazzeno *et al.*⁵¹ of the Southern Regional Research Laboratory in the U.S.A., who worked with methylolmelamine; it was again found that the amount of added resin is somewhat critical, and there is a limit beyond which the effect of the sodium hydroxide cannot be realised. Above 10.5% of added resin, the swelling action of the alkali is restricted to such an extent that it cannot achieve its purpose, and experiments were limited to approx. 8% of added resin.

The concentration of mercerising alkali covered a range of 5-30%, and although the greatest improvement was obtained with 30% NaOH (66°Tw.), difficulties were experienced because the shrinkage was so great that the edges of the samples were ripped from the pin-frames; hence 20% NaOH solution (46°Tw.) was preferred in the experimental work in the laboratory.

The time of treatment for maximum shrinkage was found to be 5 min., but actual experiments

TABLE XI
Effect of Sodium Hydroxide on Resin-treated Fabric

Treatment	NaOH (%)	Wet Rip (lb.)	Wet Abrasion (cycles)	Recovery (%)	Nitrogen (%)
Untreated		1.8	456	165	0
Melamine-formaldehyde	0	0.9	192	258	4.5
	5	1.0	196	261	4.1
	10	1.0	250	246	4.0
	13	1.1	342	245	3.8
	16	1.2	297	241	3.7
	20	1.3	414	240	3.4
	30	1.5	599	234	2.9

TABLE XII
Mercerisation without Shrinkage⁵¹

Premercerised	Resin-treated	Postmercerised	Rip Wet (lb.)	Abrasion Wet (cycles)	Crease-recovery (%)
—	—	—	1.8	456	165
—	X	—	1.0	154	257
—	X	X	1.2	245	242
X	X	—	1.2	127	269
X	X	X	1.2	271	248

were allowed a period of 20 min. to ensure the full effect beyond any doubt.

Under these conditions the ripping strength (Elmendorf) was increased 35%, and the abrasion resistance (Stoll) was doubled, in comparison with the crease-resisting fabric which had not been aftermercerised. Although the nitrogen content fell to about 3% from 4.4% in the resin-treated control fabric, there was little loss in the crease-recovery; combined recovery figures of warp and weft were 258° in the resin-treated fabric and 240° when aftermercerised (Table XI), but it is not stated⁵¹ whether the latter was obtained immediately after treatment and without being allowed to "age" to the maximum.

The area shrinkage of the resin-treated sample during mercerising amounted to 80% of the area shrinkage of the original fabric under similar conditions; the area shrinkage of the latter was about 24%. However, when the relation between ripping strength and shrinkage was corrected for area, to compare the values on a basis of equal weight, it was found that the amount of shrinkage had no significant effect on ripping strength. Improved ripping strength was achieved on samples which were not allowed to shrink during the aftermercerisation treatment, although in actual fact there would be about 4% area shrinkage.

During the experiments of Reid and his colleagues⁵¹ on aftermercerising without shrinkage, the opportunity was taken of comparing the effects of pre- and post-mercerisation, the latter being found to confer more benefit than the former (see Table XII).

The great improvement resulting from postmercerisation of resin-treated goods was never satisfactorily explained, although it may be associated with the disorientation of the originally highly orientated cellulose⁵²; the Philadelphia Section of the AATCC has stated that "aftermercerisation is well known, though not perhaps completely understood"⁵³.

On the basis of the entanglement theory, however, with three types of junction points—normal, heat-formed, and resin-formed—it seems clear that the normal hydrogen bonds and the heat-formed hydrogen bonds between the cellulose chain-molecules are broken by alkali of mercerising strength, but the cellulose-resin-cellulose bonds remain unbroken. The alkali is able to penetrate into a substantial part of the structure, which is opened to form more amorphous cellulose as the linen or cotton shrinks under no external restraint; the increase in the proportion of amorphous cellulose is confirmed by X-ray measurements. Hence the postmercerised product contains more free molecular chains and is therefore stronger, less brittle, and more absorbent. If one is permitted to coin a phrase, it has been "caustic-conditioned".

THE STEAM CURE

The probability that an excessive amount of reticulation, or a very tight network system; was responsible for some of the embrittlement of treated rayon led the writer to investigate the use of superheated steam as a medium for the final condensation of the resin. It was demonstrated qualitatively that the final cure in steam gave a product with a resistance to abrasion much superior to that obtained when dry curing was employed under otherwise comparable conditions. It appeared that the effect was due to the presence of moisture preventing the formation of hydrogen bonds between many of the hydroxyl groups which are normally separate but become bonded at temperatures above 100°C. in a dry atmosphere.

A simple method for estimating the amount of steam in the heating chamber, devised by Blease and greeted with exasperation and delight, enabled these observations to be put on a proper quantitative basis, and as a result it was possible to show a linear relation between the improvement in resistance to abrasion of steam-cured fabrics over dry-cured fabrics and the amount of steam present⁵⁴ (see Table XIII).

TABLE XIII
Abrasion Resistance of Viscose Rayon

Steam in Heating Chamber (%)	Improvement in Abrasion (%)
0	0
23	3
35	13
49	37
65	70
73	86
78	96
92	108

In the above series of trials, the added resin in the fabric was approx. 16%. Further data show the effect of heating in substantially 100% of steam on a fabric of 100% spun rayon and on a fabric with filament rayon warp and cotton weft (Table XIV). The improvement in resistance to abrasion over the products submitted to dry heat persisted over a period of more than six months, and was not removed by a series of washings.

The fact that similar improvements take place with resins other than urea-formaldehyde, including the reactant "resins", is evidence in support of the view that the process operates on the cellulose as such and not on the resin.

The effect of the steam cure on cotton is quite definite, but is not as pronounced as with rayon. On the hypothesis of the limitation of hydrogen-bonding, this might be expected, for there is much less amorphous cellulose in cotton.

It is interesting to note that resistance to abrasion is affected by the steam cure or by after-mercerising. This is in agreement with the proportion of molecular chains unrestricted by heat-formed hydrogen bonds, for the hydroxyl groups may have been prevented from bonding by the presence of steam or freed later by "caustic conditioning".

It sometimes happens that, with cotton goods which have been steam-cured, the crease-recovery is very slightly below that obtained in an atmosphere free from steam. This does not obtain with mixtures of methylolmelamine and methylolurea, and is an interesting example of synergistic behaviour.

The steam cure is really effective only within certain temperature limits. At relatively low curing temperatures, the steam molecules place themselves around the polar groups of cellulose and effectively "neutralise" many of them from hydrogen bonding, but as the temperature rises it seems probable that the energy and amplitude of vibration will increase, so that hydrogen bonding may become easier.

General

The views of the writer on the general crease-resisting phenomena, formulated in 1937, included

crease-recovery by drying and by various chemical treatments in one picture of molecular entanglement or reticulation. A widening of the old hypothesis to include the more recently expressed concept of junction points in the amorphous regions of cellulose enables heat-formed hydrogen bonds to supplement the resin bonds in the general picture.

This is in agreement with the differences between unmercerised treated cotton and mercerised treated cotton, between treated cotton and treated cotton which has been aftermercerised, as well as the differences between dry-cured goods and steam-cured goods; it is suggested that the differences are due to the proportions of normal hydrogen bonds, heat-formed hydrogen bonds, and cellulose-resin-cellulose bonds.

The fact that the nature of the cellulose-resin-cellulose bond has not been discussed in any detail must not be taken to mean that the writer has no views on the subject: it is not considered to be of prime importance in the general theory. Nevertheless, it may be stated that water-imbibition may be an unreliable index of covalent cross-linkage, as has been indicated in the present paper: there are many examples in cellulose chemistry of reduced water-imbibition without cross-linkage and also of increased water-imbibition with covalent cross-linkage, according to the swollen or collapsed state of the fibre when the linkages were formed between the molecular chains of the cellulose.

Nor has a really satisfactory explanation been forthcoming for the "ageing" of crease-resisting goods, when the initial recovery continues to improve for 7-14 days after the original treatment. It may be that the system requires time to adjust itself to the presence of the resinous infarct—as with other systems and other infarcts—and that this readjustment includes hydrogen-bonding between free hydroxyl groups in the cellulose and carbonyl and primary and secondary amino groups in the imperfect network of the resin, supplementing the hydroxyl-hydroxyl hydrogen bonds.

In addition to the entanglement theory formulated by the writer in 1937 and published in 1946⁵⁵ the mechanism of the effect has been discussed by Landells⁴⁴. The old idea of covalent cross-linkages, originally suggested by Meunier and Guyot⁵⁶ to explain the reduced swelling of methylenecellulose, has been revived and generalised by Cameron and Morton⁵⁷. A very useful review of crease-resistance and cotton was made by Buck and McCord⁵⁸, a number of valuable suggestions have come from Smith³², and a stimulating discussion of many of the controversial issues has been published by Nuessle, Fineman, and Heiges⁵⁹.

The views expressed by the writer are not intended to be controversial or pontifical: in the

TABLE XIV
Effect of Steam Cure

Fabric	Added Resin (%)		Steam (%)	Abrasion (cycles)		
	Dry	Steam		Untreated	Dry	Steam
Spun rayon	14.5	13.7	97	730	330	710
Rayon-cotton	14.3	14.3	95	855	400	858

main, differing theories come from regarding different aspects of the same facts; according to the point of view, some facts are in the foreground, while others are in the background, and some may be out of sight.

* * *

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1 BOWER ROAD
HALE
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(MS. received 25th March 1959)

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Discussion

Mr. A. R. SMITH: What is the function of the catalyst in the crease-resist process?

Mr. MARSH: The function of the catalyst is not easy to understand, but it is obviously much more than the provision of hydrogen ions. The reaction, whatever it may be, seems only to occur when the fabric is dry; furthermore, there is a temperature of about 130°C. below which no increase in time or catalytic activity appears to operate. Metallic salts, often in substantial amounts, are stated to give a "harder cure", and this is a further difficult point, unless there is some bonding effect of the bivalent metal or similar action.

A recent catalytic system has been introduced by J. J. Ryan and P. J. Taylor of Tootal Broadhurst Lee Co. Ltd. (*Australian Patent* 218,413 of May 1959); a typical example is magnesium dihydrogen phosphate, which deposits the mono-hydrogen salt from solution on heating and/or concentrating, thus causing a sudden fall in pH.

Mr. F. FARRINGTON: What is the difference between dry recovery and wet recovery?

Mr. MARSH: In the conventional self-smoothing fabrics, the difference between wet- and dry-recovery may be attributed to the breakdown of many of the hydrogen bonds on wetting; the relation is roughly 90% for cotton and 66% for viscose rayon, according to their accessibilities to resin and to water.

There has been some revival of interest recently in fabrics which possess only wet recovery; they are mainly produced by treatment in the wet state, and much of the effect is implicit in the work of F. C. Wood (*J.S.C.I.*, **50**, 411 (1931)). A modern view might be that, as the structure is swollen and

H. B.,
(1958).

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the reagent is not telescopic, the number of bonds will be small and they will be nearer the crystallite; hydrogen bonds will be less effective as they will not all have re-formed. The final network is distended and somewhat disrupted; the fundamental difference is probably one of bond-distribution. For example, V. Tripp (private communication) has shown that wet-recovery cottons fibrillate whereas dry-recovery cottons do not.

Many monofunctional reagents will produce wet recovery, and as this property may also be imparted without the formation of a chemical compound, it may depend to some extent on the degree of isotropy in the treated fibre. Some wet- and dry-recovery processes operate in two stages; priority in this field is due to Hunt and Marsh of Tootal Broadhurst Lee Co. Ltd. (B.P. 727,882; 727,888;

727,889; and 727,890). Most wet-recovery treatments impart wet recovery only and the dry recovery may be very poor; the dry-recovery processes may give good dry recovery and good wet recovery.

Prof. E. ELÖD: The physical properties of native and regenerated cellulosic fibres containing aminoplasts depend essentially on the distribution of the resin in the fibre. The resin normally lies mainly in the outer layers (skin) of the fibres and causes insufficient resistance to abrasion. We succeeded in fixing most of the aminoplast in the core of the fibres by *shock* action. On condensation at room temperature for several weeks in a closed container, the same result was obtained, but the washability became insufficient. Perhaps at lower temperatures the simultaneous formalisation of cellulosic fibres does not take place.

CORRESPONDENCE

The Publications Committee does not hold itself responsible for opinions expressed by correspondents

Changes of Colour caused by Fluorescent Brightening Agents

I read with interest the letter under the above heading by Ward and Blackburn¹. May I ventilate another problem caused by these newcomers to the range of textile auxiliaries?

Fluorescent brightening agents are now used to such an extent that white fabrics are no longer white, but coloured to innumerable hues of pale purple, pink or blue. In fact, a white fabric now decidedly falls into the category of dyed fabrics, without however being recognised as such by either manufacturer or user. Great problems are created in the fabric-consuming industries through shades varying from delivery to delivery, or even

from piece to piece in one delivery. When representations are made, one is invariably informed that nothing can be done.

Has the finishing industry really come to this impasse? What finisher would dare not to match any pastel shade to pattern? Yet pastel whites are thrust upon the user indiscriminately. Is nobody going to do anything about it?

E. KORNREICH

TECHNICAL DEPARTMENT
TRUBENISE (GT. BRITAIN) LTD.
39 PARK STREET
LONDON W.1

18th November 1959

¹ Ward, J. S., and Blackburn, D., J.S.D.C., 75, 493 (Oct. 1959).

Notes

Society Honours

At its meeting on 2nd December, 1959 Council made the following awards—

<i>Honorary Member</i>	C. Paine
<i>Perkin Medal</i>	C. J. T. Cronshaw J. T. Marsh
<i>Gold Medal</i>	I. D. Rattee W. E. Stephen H. Ris
<i>Silver Medal</i>	H. F. à Brassard G. G. Bradshaw J. W. Reidy N. Hamer
<i>Bronze Medal</i>	W. R. Leigh J. Rayment

Presentation of these awards, the citations for which appear in the appropriate Medals and Awards notices on page 4 of this issue, will take place at the Annual Dinner in Leeds on Friday 29th April 1960.

Election of Fellows

At the Council meeting held on 2nd December 1959 the following were elected Fellows of the Society—

Frederick Victor Davis

Bolton, Lancashire; Director, James Hardcastle & Co. Ltd.

Sidney Milton Edelstein

New York; Technical Director and President, Dexter Chemical Corp'n.

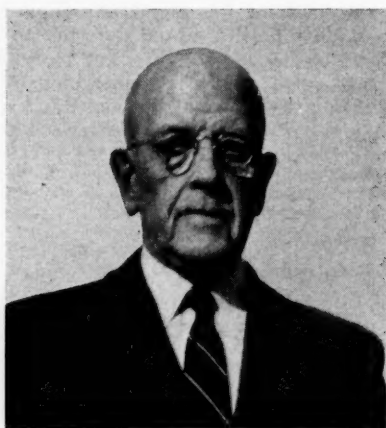
Louis Jack Sheps

Lachine, Quebec; Vice-President, Director of Research, Trilon Chemicals Ltd.

William Hamlin Cady

Presentation of Scroll of Honorary Membership

The illuminated address of Honorary Membership of the Society (see J.S.D.C., 75, 350 (1959)) was presented to Mr. Cady by Dr. W. G. Parks of the University of Rhode Island and a Vice-president of the A.A.T.C.C. at a meeting of the Rhode Island Section of the A.A.T.C.C. on 29th September 1959.



Mr. Cady, an A.M. of Brown University and a Fellow of the Society, of which he has been a member for over 50 years, is a Past President of the A.A.T.C.C. which awarded him the Louis A. Olney Medal in 1946. After his retirement from industry, where for many years he was the Chief Chemist of the U.S. Finishing Company, he became the editor of many A.A.T.C.C. *Technical Manuals and Year Books*. As Chairman and Co-ordinator of the A.A.T.C.C. Colour Index Editing Committee 1946-57 he played one of the leading parts in the preparation of the Second Edition of the *Colour Index*. It is hoped that he will have many happy years in which to enjoy the honours that he has so worthily earned from both the Society and the A.A.T.C.C.

Death of Member

We regret to report the death of Mr. J. Donaldson.

A.S.D.C. Examination 1960

The annual examination for the Associateship of the Society of Dyers and Colourists will be held on Thursday, Friday, and Saturday, 16th, 17th, and 18th June 1960. Candidates may take Papers A and B together, followed in a subsequent year by C, D, and either E(i) or E(ii); or Papers A, B, and C may be taken together and D and either E(i) or E(ii) subsequently. Candidates must indicate the special branch of tinctorial technology in which they desire to be examined and state whether they intend to take the examination in one or two stages and which of the two papers E(i) or E(ii) they will take.

Application forms can be obtained from the offices of the Society and must be completed and returned not later than Saturday, 19th March 1960.

Colour Index

Meeting of the British and American Editors

The *Colour Index* Editorial Board held a meeting with Mr. W. D. Appel, Chairman and Co-ordinator of the *Colour Index* Editorial Committee of the A.A.T.C.C., who was accompanied by Mr. G. Paine, Executive Secretary of the A.A.T.C.C., in the Society's Library on 23rd September 1959. Thorough survey was made of and complete agreement reached on the policy and the working arrangements to be carried out in the collecting, compiling, and editing of the material to be included in supplementary volumes.

Historical Notes on the Waste Silk Spinning Industry in Yorkshire with special reference to Messrs. Ford Ayrton & Co. Ltd.—Low Bentham

The Society through its Committee for the Preservation of Historical Records is indebted to Mr. H. Wilkinson, formerly head of the Dyeing Department of Huddersfield Technical College and now of Preston, Lancashire, for a beautifully prepared folder of historical notes on the Yorkshire silk industry with special reference to Messrs. Ford Ayrton & Co. Ltd., Low Bentham.

After describing the beginning of the silk industry in Yorkshire some 90 years ago Mr. Wilkinson traces its migration along the railway line from Leeds to Lancaster. The notes include descriptions of the various types of raw materials and many of the uses to which the finished yarns were put.

Other sections deal with the machinery employed and with the chemical processes involved, e.g. scrooping, bleaching, and white dyeing.

Particularly interesting are the details of the wages paid and of the profit-sharing and co-partnership schemes in operation as far back as 1919.

The appendices contain excellent photographs of the works and machinery at Low Bentham as well as patterns of silk plushes.

In a pocket in the back cover are a number of booklets issued by Messrs. Ford Ayrton over the years telling the interesting story of silk and of the firm and its profit-sharing co-partnership scheme.

This interesting folder may be seen at the offices of the Society by arrangement.

Worshipful Company of Dyers of London Election Prime and Renter Wardens

A General Court of the Company has elected Mr. Richard Francis Rothwell, T.D. as Prime Warden and Mr. Aubrey Colin Milward Harding as Renter Warden.

Convocation of the Textile Institute 1959

At this Convocation held on 3rd November 1959 in Manchester several members of the Society received awards among them being Institute Service Medals to Walter Garner and Alexander Robert Urquhart.

University of Bombay Silver Jubilee of the Department of Chemical Technology

The Department of Chemical Technology of the University of Bombay commenced its work on 4th August 1934 and celebrations in honour of its silver jubilee have been held during the first week of January 1960. During the whole of its existence the Department has had a course in textile chemistry and in 1943-5 instituted courses in the technology of intermediates and dyes and the technology of pigments, paints, and varnishes. Courses in other technologies, e.g. chemical engineering and plastics, have also formed part of the Department's activities. In commemoration of this event a Silver Jubilee Fund has been created; it will be mainly utilised to improve the facilities for research and activities concerned with student welfare.

16th All India Textile Conference and Industrial Exhibition

This conference and exhibition, organised by the Mysore Branch of the Textile Association, India, were held in Bangalore on 24-26th May 1959 and had an attendance of nearly 600. Abstracts of papers read that were of interest to members of the Society appear in the Abstracts Section of the *Journal*.

U.S. Federation of Paint & Varnish Production Clubs

Joseph J. Mattiello Memorial Lecture 1959

This lecture, instituted to commemorate Dr. Joseph J. Mattiello, was given recently at the 37th Annual Meeting of the Federation of Paint and Varnish Production Clubs held at Atlantic City, N.J., by Vincent C. Vesce on "Exposure Studies of Organic Pigments in Paint Systems". Copies of the lecture can be obtained from Allied Chemical International, National Aniline Division, 40 Rector Street, New York 6, N.Y.

Third International Congress on Surface Activity

This congress will be held in Cologne on 12-17th September 1960. Full information regarding it can be obtained from Generalsekretariat des III. Internationalen Kongress für Grenzflächenaktive Stoffe, Koblenzer Strasse 232, Bonn/Rhein, Germany.

C.S.I.R.O. Process for Producing Washable Non-iron Woollen and Worsted Fabrics "Sironized" Australian Certification Trade Mark

Details of the above process were published at a meeting of Australian wool manufacturers in Geelong on 4th September 1959. Copies of these details and of C.S.I.R.O. Reports No. G8 and G9 giving details of the shrink-resisting and setting processes for producing washable, non-iron effects in pure wool fabrics may be obtained from the International Wool Secretariat, Dorland House, 18-20 Regent Street, London, S.W.1. Fabrics treated by this process will be on sale in Australia this spring. The process will be controlled in Australia under the certification trade mark "Sironized". Arrangements for the use and control of the process outside Australia are still under discussion.

Manchester College of Science and Technology Lectures on Modern Dyeing Machinery including Continuous Processes

A course of 9 lectures on the above subject will be held on Tuesday evenings commencing 2nd February 1960. The fee for the course is thirty shillings. Full details and enrolment forms are obtainable from the Registrar, The Manchester College of Science and Technology, Sackville Street, Manchester 1.

Meetings of Council and Committees December 1959

Council—2nd

Fastness Tests Co-ordinating—1st

Terms and Definitions—11th

Publications—15th

Finance and General Purposes—30th.

COLOUR INDEX

Corrections

January 1960

VOLUME 1

Page					
1125	delete	C.I. Acid Red 78			
		transfer dye and all information to			
1130		C.I. Acid Red 88	for	C.I. Acid Red 88	
			read	Roccelline NS KKK
1199		C.I. Acid Violet 17	transfer	Roccelline NS NSK
			to	Wool Violet 4BN NAC
1305	delete	C.I. Acid Blue 173		C.I. Acid Violet 49	
		transfer dye and all information to			
1387	delete	C.I. Acid Black 33		C.I. Direct Blue 1	
		transfer dye and all information to			
1413	delete	C.I. Mordant Yellow 15		C.I. Acid Black 24	
		transfer dye and all information to			
1438	delete	C.I. Mordant Orange 11		C.I. Mordant Yellow 1	
		transfer dye and all information to			
1473	delete	C.I. Mordant Red 53		C.I. Mordant Orange 1	
		transfer dye and all information to			
1474	delete	C.I. Mordant Red 57		C.I. Mordant Red 19	
		transfer dye and all information to			
1510	delete	C.I. Mordant Blue 16		C.I. Direct Red 1	
		transfer dye and all information to			
1546	delete	C.I. Mordant Green 37		C.I. Mordant Blue 7	
		transfer dye and all information to			
1564	delete	C.I. Mordant Brown 32		C.I. Mordant Green 14	
		transfer dye and all information to			
1583	delete	C.I. Mordant Brown 83		C.I. Mordant Brown 24	
		transfer dye and all information to			
1589		C.I. Mordant Black 9	transfer	C.I. Mordant Brown 60	
			to	Sunchromine Black P2B NSK
				C.I. Mordant Black 7	

VOLUME 2

2003		C.I. Direct Yellow 1	transfer	Nippon Yellow CT NSK
			to	C.I. Direct Yellow 24	
2027		C.I. Direct Yellow 57	transfer	Solamine Fast Yellow 3RLN FW
			to	C.I. Direct Yellow 34	
2039		C.I. Direct Orange 7	transfer	Nippon Orange GG NSK
			to	Direct Orange 6	
2224		C.I. Direct Blue 151	transfer	Japanol Copper Blue 2B NSK
			to	C.I. Direct Blue 168	
2278		C.I. Direct Brown 39	transfer	Nippon Brown BC NSK
			to	C.I. Direct Brown 44	
2295		C.I. Direct Brown 95	for	Solamine Fast Brown BSW FW
			read	Solamine Fast Brown BRL FW
2331		C.I. Direct Black 18	transfer	Columbia Black EP FW
			to	C.I. Direct Black 38	
2525		C.I. Vat Green 9	for	Nihonthrene Black BBN NSK
			read	Nihonthrene Black BB NSK
2651	delete	C.I. Azoic Red 44		C.I. Azoic Red 28	
		transfer dyes and all information to			
2665	delete	C.I. Azoic Blue 17		C.I. Azoic Blue 7	
		transfer dye and all information to			
2665	delete	C.I. Azoic Blue 18		C.I. Azoic Blue 9	
		transfer dye and all information to			
2687		C.I. Oxidation Base 11	transfer	Fouramine OP Fran
			to	C.I. Oxidation Base 17	
2835		C.I. Solvent Orange 7	for	m.p. (recryst.) 133°C	
			read	m.p. (recryst.) 166°C	

VOLUME 3

3029	under 12140	for	M.p. (from glacial acetic acid) 133°C	
		read	M.p. (from glacial acetic acid) 166°C	
3094	under 17125	for	C.I. Mordant Green 32 (Dull green)	
		read	C.I. Mordant Green 14 (Dull green)	
3503	under 62080	for	Solubilities. See Solvent section (Vol. 2, p. 2877)	
		read	Solubilities. See Solvent section (Vol. 2, p. 2876)	

OBITUARY NOTICE

Fred Smith, F.S.D.C.

Fred Smith was born in 1886 at Cliffe House, Bruntcliffe, the youngest son of Robert Dixon Smith, founder of the family business. He was educated at Wheelwright Grammar School, Dewsbury, Leeds Grammar School, and the Yorkshire College. Following a brief apprenticeship elsewhere, he joined William Smith and Sons soon after the turn of the century as a dyer and remained with them until, as Chairman, he saw the transfer of the family concern from a private to a public company in 1956. He remained active, as a director, until his death on 6th October 1959.



At the age of 28, Fred Smith joined the Society of Dyers and Colourists; within a year he was serving on the West Riding Committee and from that time until his death he occupied an unbroken and impressive sequence of positions in the Society. These included every aspect of the Society's work and there is scarcely a single standing Committee on which Mr. Smith had not at some time served. In 1954 he was declared President-Elect of the Society and the untimely death of Mr. F. L. Goodall saw Mr. Smith's accession to the Presidency in mid-term of that year. In the whole history of the Society of Dyers and Colourists there has probably been no other member who identified himself so completely with its life and there can be very few members, in any part of the world, who did not know Fred Smith.

Fred Smith always grasped fully the purposes for which the Society of Dyers and Colourists exists. For him the first of these was "to help make better dyers". He himself remained engaged in the pursuit of knowledge about his craft up to the day of his death and regarded this as the normal state of mind for anyone else. And though he regularly and often brusquely disclaimed any leanings towards the academic view of anything at all, his knowledge embraced always the essence of what was new, and what was important in what was new. This most striking characteristic reflected more than the Yorkshire shrewdness which Fred himself might on occasions claim, with due pride, to possess; he had a highly integrated knowledge of his trade plus a degree of intuitive wisdom which in other spheres would be admired as unusually acute scientific insight. His anxiety that all dyers should be seekers after knowledge—and that all young members of the craft should be fitted properly for the search—was the spring of his interest in the Diplomas scheme, which scheme reached its final stage of established practice during his own Presidency.

Fred was a great traveller. His journeys tended to be oriented by the desire "to go and find out for myself". Thus dye makers and machinery manufacturers all over the Continent were subject to Smithsonian inquisition at fairly regular intervals and especially if they were known to have any newly developed products or ideas. The writer knows of more than one distinguished house who always looked forward to the experience "not for what Fred Smith took from here so much as for what he brought with him" to quote one such.

With the exception of a single year, Fred Smith continued to serve on Council, in one capacity or another, from 1921 to 1959. In 1947 he was rewarded with the Society's Gold Medal, given for truly exceptional services, and in 1956 became an Honorary Member.

Beyond his good fellowship, generosity to younger people, and those obvious qualities which made him so many friends all over the world, was another quality—apparent perhaps only to those who knew him intimately: *courage*. Fred Smith had a share of personal tragedy more than most of us are asked to bear. Almost never was this apparent in his demeanour. On the contrary, he always lived up to one of his favourite sayings: "if you want owt from life you must put summat in". To have observed the process of Fred Smith putting something into life over the last twenty-five years has been a high privilege and, especially for one of his younger friends, something of an inspiration.

JOHN BOULTON

New Books and Publications

Silk Screen Techniques

By J. I. Biegeleisen and M. A. Cohn. Pp. iv + 187 + 8 colour illustrations. New York: Dover Publications Inc. 1958. Price, \$1.45.

This is one of a series of books on art, and though the preface states that it "encompasses the entire range of stencil techniques as a fine art and commercial printing process", it is purely an art or craft book dealing primarily with the reproduction on paper of artists' paintings and drawings, on a "Do-it-yourself" basis. The only reference to textile usage is a two-sentence one in the first chapter, remarking that miles of cloth are screen printed.

The first chapter, "Origins and Development" suggests that screen methods for reproducing paintings originated with a group of American artists in 1938, but Mackenzie (J.S.D.C., 54, p. 196 (1938)) speaks as if they were established and accepted methods at that date, and indeed were probably used by the Polygraphia Society in 1830-1840 for the reproduction of "Old Masters".

Succeeding chapters give instructions, with diagrams, for making small screens by the known hand methods and by photography. Here the "direct" method used by textile printers is dismissed as a "long procedure" with "an almost impossible task to dissolve the gelatin-coated screen" (presumably the gelatin from parts where it is not wanted). Directions are given for the "transfer" process using photo-stencil film similar to Autotype tissue. There is no indication of the chemical nature of the sensitising bath; one is asked to buy it ready-made from a supplier. A chapter on "Multicolour Printing" deals with elementary registration principles, and one on "Colour" is concerned almost entirely with ready-mixed oil paints, varnishes, and tempera colours. The final chapter describes making prints on paper from the screens.

The instructions and diagrams are clear, and would enable a beginner to make a start on a craft basis. But the textile printer would learn nothing from it, and such matters as the use of dyes and thickenings for aqueous media, modern industrial screen-making techniques, designs produced "in repeat" and the problems of printing continuous lengths from them, are quite outside the scope of the book.

F. V. DAVIS

Věda a Výzkum v Průmyslu Textilním Sborník Přednášek z II Koloristického Sjezdu v Tatranské Lomnici 1957

Prague: Czechoslovakia Ministerstvo Spotřebního Průmyslu. 1958. Pp. 155.

The first national conference of the Czechoslovak dyestuff and textile chemists was held in 1955 and attended by 430 experts. It was then decided to organise in 1957 a conference on a wider basis to which delegates and guest speakers from Russia and other communist countries would be invited.

The present booklet is a collection of fourteen of the more important papers presented at the 1957 conference which was attended by 280 experts including delegates and speakers from Russia, Poland, East Germany, Hungary, Roumania, and Bulgaria. Summaries are given in Czech, Russian, German, and English.

The application of carriers to the dyeing of polyester fibres is described in three not dissimilar papers. The Czechoslovaks favour butyl salicylate as carrier. The field of carrier dyeing is now more than adequately covered by a vast literature but very little fundamental and practical progress is being achieved. The papers of this conference only slightly modified and enlarged on known facts.

The use and chemistry of epoxy resins and their condensation products with polyamines as binders for pigments in printing and dyeing are described by two independent workers. These papers should provoke considerable interest. The printing emulsions are of the oil-in-water type, the emulsifiers used being acetates, formates or lactates of low molecular weight precondensates of polyamines with epoxyethers of bisphenolpropane. These emulsifiers, besides acting as stabilisers, take part in the condensation reaction and do not affect the wet-fastness properties of the resulting films. They provide excellent adhesion even on non-polar surfaces. It is claimed that the method is particularly suitable for the continuous dyeing of glass fibres with pigments.

Experts from the Czechoslovak hat industry contributed a study on the dyeing of mordanted fur by acid dyes. It is shown that only products with monosulphonic acid groups give level dyeings. The dyeing of Woleryon, the East-German polyacrylic fibre, is described.

The wide scope of the conference is shown by the fact that it included papers ranging from newer constructions of roller printing machines—a subject often neglected in our own symposia—to purification of waste-water from dye makers. It is suggested to diazotise the waste waters from one plant and to couple them with passive components contained in the waste-waters of other plants.

One of the papers submitted by Russian experts deals with the photocatalytic degradation of cellulosic fibres by certain vat dyes. The degree of degradation is measured by quantitative estimation of carbonyl groups rather than of carboxylic groups. The basis of the method is the reduction of an alkaline silver thiosulphate solution. Effect of substituents on the photoactivity of a number of yellow vat dyes is studied but no unequivocal conclusions have yet been reached.

It is interesting to read in the introduction to the booklet that about fifty years ago a small circle of Czechoslovak textile printers founded a small professional society which was soon afterwards to develop into the International Society of Chemists and Colourists.

P. KRUG

The Sequestration of Metals

Theoretical Considerations and Practical Applications

By Robert L. Smith. Pp. vii + 256. London: Chapman & Hall Ltd. 1959. Price, 42s. 0d.

After a fairly exhaustive discussion of the definition of sequestration, there are chapters on valency and basicity; the chelating ring and the influence of metals and ligands; stability of chelates and competition in chelate systems; chemical and physical properties of sequestering agents; application of sequestering agents; applications in industry; applications in analytical chemistry; applications in applied biology; future developments; author and subject indices.

The author has chosen to write in a familiar style, but it is a pity that he has decided not to pay too much attention to formal grammar and brevity. This book is not addressed to those

carrying out research in the field, so that the chapter on valency and basicity is meant to be a detour around the more difficult concepts of wave mechanics. It is questionable whether the reader will benefit from this chapter which contains a number of misleading statements. For example, there is some confusion between magnetic and dipole moments, and it is stated that the formation of a chromium complex of E.D.T.A. involves a rearrangement of the inner orbits.

It was the intention of the author to produce a general book dealing with the subject of sequestration in all its aspects, and in this he has achieved a considerable degree of success. The book is well produced and mis-prints are few, but the one on page 11 will certainly confuse "chemists of the variety to whom this book is addressed".

E. V. TRUTER

New Books Received

Techniques of Polymer Characterization. P. W. ALLEN (editor). London and New York: Butterworths Scientific Publications and Academic Press Inc. Pp. xiv + 256. 50s. 0d. (\$9.50).

British Chemicals and their Manufacturers 1959. London: Association of British Chemical Manufacturers. Pp. ii + 207. Gratis.

Silk Screen Techniques. J. I. BIEGELEISEN and M. A. COHN. New York and London: Dover Publications Inc. and Constable & Co. Pp. iv + 187 + 8 colour illustrations. 1958. \$1.45.

List of Periodicals and Serials in Science, Commerce, and Technology. Bradford: Central Public Library. Pp. ii + 47. July 1959.

High Temperature Laundering of Woollen Hospital Blankets. J. C. DICKINSON, R. E. WAGG, and G. D. FAIRCHILD. London: British Launderers' Research Association and The International Wool Secretariat. Pp. 25. June 1959. No price.

Annual Reports on the Progress of Chemistry for 1958. Volume LV. London: The Chemical Society. Pp. 527. 1959. 40s. 0d.

International Conference on Co-ordination Chemistry. Special Publication No. 13. London: The Chemical Society. Pp. iii + 204. 1959. 42s. 0d. (\$6.00).

Measuring and Predicting the Generation of Static Electricity in Military Clothing. Textile Series Report No. 110. A. M. CRUGNOLA and H. M. ROBINSON. Natick, Massachusetts: United States Army, Headquarters, Quartermaster Research and Engineering Center, Textile Clothing and Footwear Division. September 1959. Pp. vi + 64 + ii illustrations. No price.

Lehrbuch der Organischen Chemie. PAUL KARRER. Stuttgart: Georg Thieme Verlag. 13th edition 1959. Pp. xx + 1057. DM 60.00.

Filmdruck—Rapport, Farbauszüge, Schablonen. RICHARD KÜNZL. Textheft pp. 84. Bildheft pp. 75. Stuttgart: Konradin-Verlag Robert Kohlhammer GmbH. 1959. DM 18.90.

Rapportrichtiges Musterzeichen. RICHARD KÜNZL. Stuttgart: Konradin-Verlag Robert Kohlhammer GmbH. Pp. 56. 1959. DM 8.50.

Ageing of Rubber: Effects of Metal Contamination. B. N. LEYLAND and R. L. STAFFORD. (Reprinted from *Trans. Instn. Rubber Ind.*, 35, 25-44 (April 1959).) Manchester: Imperial Chemical Industries Ltd. Dyestuffs Division.

Aspects Scientifiques de l'Industrie Lainière. F. MONFORT. Paris: Dunod Éditeur. Pp. xviii + 514. 1960. Francs 7,000.

Shrinkage—A Survey of Shrinkage Problems and their Solutions with special reference to Industrial Overalls. Liverpool: Overall Manufacturers' Assocn. of Great Britain. Pp. ii + 42. Aug. 1959. 5s. 0d.

Fiber to Fabric. M. DAVID POTTER and BERNARD P. CORBMAN. London and New York: McGraw-Hill Publishing Co. Ltd. and McGraw Hill Book Co. Inc., Gregg Publishing Division. 3rd edition 1959. Pp. x + 342. 33s. 0d.

Forschungsberichte des Wirtschafts- und Verkehrsministeriums Nordrhein-Westfalen. No. 501. Untersuchungen in der Leinengarnbleiche. WALDEMAR ROHS and INGEBORG GEURTEN. Opladen: Westdeutscher Verlag. Pp. 37. 1958. DM 11.50.

Register of Fellows and Associates, 1958, with a Supplementary List of Graduate Members. London: The Royal Institute of Chemistry. Pp. xx + 576. Oct. 1958.

Geographical Index to the Register of Fellows and Associates, 1958. London: The Royal Institute of Chemistry. Pp. 96. Oct. 1958.

Index of Chemistry Films. A Comprehensive List of Films and Filmstrips on Chemistry and Related Topics. London: The Royal Institute of Chemistry. Pp. ix + 150. 1959.

Forschungsberichte des Wirtschafts- und Verkehrsministeriums Nordrhein-Westfalen. No. 496. Farberische Eigenschaften von der Herstellung von Verdickungen in der Stoffdruckerei bestimmten Stoffen. PETER VOGEL. Opladen: Westdeutscher Verlag. Pp. 26. 1957. DM 9.30.

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., 68, 23 (Jan. 1952) and also, together with symbols and the periodicals abstracted, in the annual index

I—PLANT; MACHINERY; BUILDINGS

Yarn Package Drier

A. T. Shapovalov *Tekstil. prom.*, 19, 75-76 (July 1959)
A new Russian drier SKB-6 for bobbins and wound packages is described, and a working diagram given. Air at 110°C. is circulated through the packages at 9000 cu.m./hr. and 1200 mm. water pressure in a closed system. The capacity mixture content is about 1000 kg. of yarn containing 125-130% of water. The time taken for drying is 7-9 hr. G.J.K.

Washing in Open Width

A. Freyberg *Melliand Textilber.*, 40, 911-912 (Aug 1959)
Two units, "Cascade" and "Intensiva", for washing and rinsing respectively have been developed. S.M.J.

Fluidised Bed in Textile Processing

H. C. Jain, K. Manivaman, J. Varghese, P. N. Sharma, R. Sathapaty, H. R. Chipalkatti, and V. B. Chipalkatti

16th All India Textile Conference and Industrial Exhibition Souvenir, 26-37 (May 1959)

An account of work done at the Shri Ram Institute for Industrial Research, Delhi, on various ways of using a fluidised bed for heating or drying textiles. Developments include a unit combining both a molten metal bath and a fluidised bed, a jet fluidisation unit and use of the treating bath itself, e.g. dye liquor, as the fluidised bath, in this latter case very much improved rate of dyeing being obtained. C.O.C.

PATENTS

Non-premix Burner for a Carbon Black Furnace
Phillips Petroleum Co. USP 2,890,746

Pelleting Carbon Black (C.I. Pigment Black 6 and 7)
Phillips Petroleum Co. USP 2,890,942

Feeding Stretchable and Shrinkable Webs

B. F. H. Mellbin BP 822,394
The drive for all the rollers is derived from the same driving shaft. It is so designed that the rollers can assume different speeds as the length of the web changes and yet keep the same tension in the web. C.O.C.

II—WATER AND EFFLUENTS

PATENT

Purification of Effluents

Filtration Consultants BP 822,749

Non-ionic Detergents in Raw Wool Scouring including Studies of Waste Clarification (VII p. 56)

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Effect of Softeners on Viscosity of Size

C. C. Shah 16th All India Textile Conference and Industrial Exhibition Souvenir, 83-86 (May 1959)

Sulphated castor oil and vegetable tallow produce colloidal instability in maize starch sizes and so cause conditions favouring aggregation with consequent rise in viscosity. Such sizes usually have poor abrasion resistance. Tamarind kernel sizes have better stability against such softeners. Soap-oil emulsions, particularly those from castor oil, cause abrupt rise in the viscosity of maize starch sizes. C.O.C.

Sriferet Urea-formaldehyde Resins and Stabaca Catalysts in Textile Finishing

K. Taneja, J. A. Masarguppi, K. V. Ramalingam, E. S. Rao, N. B. Sattur, and V. B. Chipalkatti

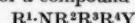
16th All India Textile Conference and Industrial Exhibition Souvenir, 1-10 (May 1959)

An account of agents developed in the Shri Ram Institute of Industrial Research, Delhi, their application in practice, and tests on finished fabrics. C.O.C.

PATENTS

Antistatic Agent

American Cyanamid Co. USP 2,891,878
A small quantity of a compound of formula—



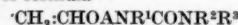
(R¹ = aliphatic or alicyclic; R² and R³ = Alk or hydroxyalkyl of 1-3 C or -(C₂H₄O)_mH (m = 2-200); R⁴ = aralkyl or hydroxyalkyl of 1-3 C or -(C₂H₄O)_mH (m = 2-200); Y = anion) and a synthetic plastic finishing material are dissolved in an organic solvent, applied and the solvent evaporated off to leave a water-insoluble transparent antistatic finish on the surface of the material treated. Thus stearamidopropyl dimethyl-β-hydroxyethyl ammonium dihydrogen phosphate dissolved in butyl Cellosolve and polystyrene dissolved in benzene are mixed together. Applied to methylmethacrylate sheeting the mixture yielded an antistatic finish which was fast to washing with soap and water. C.O.C.

Fire-retarding Additives

Chemische Werke Albert BP 822,123
Surface coating compositions, impregnating agents, etc., are rendered fire retarding by adding to them powdered condensates obtained from HCHO (1 part by wt.), urea (1.5-2.25) and ammonium orthophosphate (1.0-2.5). C.O.C.

Unsaturated Ureido Ethers and their Polymers

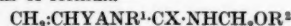
Rohm & Haas Co. BP 822,266
Compounds of formula—



(A = divalent hydrocarbon of < 19 C and places at least 2 C atoms between the O and N atoms, the hydrocarbon chain may be interrupted by O, N or S atoms; R¹ = H or a monovalent straight chain hydrocarbon of < 19 C and may contain Hal, OH or cyano groups and the chain may be interrupted by O, N or S atoms; R² = a monovalent straight chain hydrocarbon of < 25 C and may contain Hal, hydroxyamino, nitro or cyano groups and the chain may be interrupted by O, N or S atoms; R³ = H or a hydrocarbon of the type of R²; alternatively R¹ and R² together with the ureido N atom may form a morpholine or piperidine residue) unlike compounds of type CH₂:CHO-A-NR¹CONH₂ have (1) little or no activity with aldehydes, (2) lower m.p. and high vapour pressure facilitating their purification by distillation, (3) orientation at an oil-water interface, (4) modified solvent power, (5) yield polymers of greater chemical stability. Depending on their constituents they have most varied uses, e.g. as solvents, for modifying cellulose and other hydroxylic compounds, as components for resins, intermediates for textile assistants, etc. Cellulose and other polyhydroxy compounds when treated with these agents can be further reacted with formaldehyde to give them strong hydrophobic properties. C.O.C.

Polymerisable Ureido and Thioureido Compounds

Rohm & Haas Co. BP 822,267
Compounds of formula—



(Y = O or S; A = phenylene or alkylene of 2-4 C and places at least 2 C atoms between the Y and N atoms; R¹ = H, cycloalkyl or Alk of 1-12 C; X = O or S; R² = Alk) are stable under normal storage conditions but are readily polymerisable by addition polymerisation techniques to yield linear types of soluble polymers which are insolubilised by heating, preferably in presence of an acidic catalyst. They have a wide range of uses for the resin finishing of textiles, leather, paper, etc. Thus N-(2-vinyloxyethyl)-N'-methoxymethyl urea mixed with dimethylol urea is used to produce a crease-shedding, dimensionally-stable finish on rayon cloth. C.O.C.

Curing Agents for Polyepoxides

N.V. de Bataafsche Petroleum MS. BP 822,638
Hydrogenated aromatic primary or secondary polyamines containing < 2 amino H atoms are good curing

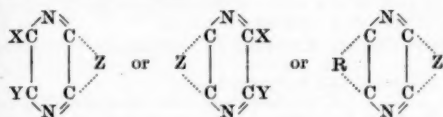
agents for polyepoxides. When the amine radicals are attached to different cycloaliphatic radicals curing can be done hot or cold but when they are attached to the same cycloaliphatic radical curing only occurs on heating. C.O.C.

Hardening Gelatin

Gevaert Photo-Produkten BP 822,061
Treating polymers containing hydroxyl groups, preferably incompletely esterified cellulose or poly(vinyl alcohol) with maleic acid or maleic acid derivatives, yields tanning agents for gelatin. C.O.C.

Driers

General Aniline BP 822,365
Compounds of formula—



(X and Y = H, Hal, OH, NO₂, COOH or aliphatic or aromatic groups; R and Z = atoms to complete a ring) are excellent driers for drying or semi-drying oils. Thus dibenzo(a,c)phenazine, acenaphthoquinoline and benzoquinoline are particularly effective when used in combination with a manganese drier. C.O.C.

Rosin Size for Paper

Hercules Powder Co. BP 822,046
The efficiency of rosin sizes is improved by giving them a topping treatment to remove 2.5–20.0% by weight of light oils, based on the weight of the rosin material, e.g. wood or gum rosin. The treated sizes are much less liable to foam. The topping may be done by fractionation at a reduced pressure or by distillation. C.O.C.

Primers for Vinyl Chloride Resin Coatings

Union Carbide Corp. USP 2,891,876
A blend of a polyurethane resin and a vinyl chloride-vinyl ester-maleic acid or anhydride copolymer is an excellent primer for obtaining adhesion of vinyl chloride plastisols to nylon and metals. C.O.C.

Opalescent Pigments for incorporation in Detergents (IV p. 49)

Properties and Application of Urethane Coatings (V p. 53)
Amylhydrosilicones as Water-repellent Finishing Agents (X p. 60)

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Chemistry in the Ancient World

J. R. Partington *Proc. Chem. Soc.*, 241–249 (Sept 1959)
Historical with some reference to dyes, pigments, and coloration processes. C.O.C.

Absorption Spectra of Coloured Solutions Produced by adding Alkali to Nitrobenzene in Acetone

T. Abe *Bull. Chem. Soc. Japan*, 32, 775–776 (July 1959)
Mononitro-, o-, m-, and p-dinitro- and 1,3,5-trinitrobenzenes all give reddish colours when treated with NaOH in acetone soln. Spectra are given, and also for addition of Ca(OH)₂ and NH₄OH to trinitrobenzene. A.J.

Rate of Colour Reaction of m-Dinitrobenzene with Sodium Hydroxide in Acetone

T. Abe *Bull. Chem. Soc. Japan*, 32, 887–888 (Aug 1959)
Nitrophenylsulphonylsulphanilil and -metanilil Chlorides with the Nitro Group in Various Positions
B. Y. Gordinskii and M. L. Shevchenko

Nauch. Zapiski L'vov. Politekh. Inst., Ser. Khim.-Tekhnol., 50, (3), 72–79 (1958); *Chem. Abs.*, 53, 17514 (25 Sept 1959)

H₂NZO₂H, CaCO₃, and O₂NXC₂(X, Y, and Z = o-, m-, and p-C₆H₄SO₂ respectively) form (O₂NXNHZO)₂Ca converted by PCl₅ and POCl₃ to O₂NXNHZCl, O₂NYNHZCl, O₂NXNHYCl, O₂NYNHYCl, and O₂NZNHYCl were similarly prepared. O₂NYNHZO₂Na and ClSO₃H form O₂NYNHZCl, O₂NYNHC₆H₄, and ClSO₃H form O₂NYNHZCl, C₆H₅SO₂NHC₆H₅ and ClSO₃H do not form the desired HZNHCl but C₆H₅SO₂Cl and H₂NZO₂H. C.O.C.

Brown Polysulphonamide Dyes for Chrome Leather

Y. P. Berkman and B. Y. Gordinskii
Nauch. Zapiski L'vov. Politekh. Inst., Ser. Khim.-Tekhnol., 50, (3), 808 (1958); *Chem. Abs.*, 53, 17514 (25 Sept 1959)

O₂NYNHZCl (Y and Z = m- and p-C₆H₄SO₂) and Direct Brown 3G do not yield a satisfactory dye as the product is not soluble enough and has little affinity for leather. 1,4-CH₃CONHC₆H₄SO₂Cl and H₂NYNHZNH₂ after being condensed together and boiled with NaOH form 1,4-H₂NC₆H₄SO₂NHYNHZNH₂Na, which diazotised and coupled with m-C₆H₄(OH)₂ forms a reddish brown dye having good affinity for leather. Diazotised H₂NYNHYNHZNH₂Na coupled with m-C₆H₄(OH)₂ yields an orange dye (brown if boiled with K₂S) and with 1-C₁₀H₇OH a violet brown (brownish beige if boiled with K₂S); they have good affinity for leather. C.O.C.

Diazo Components for Dyes whose Chromophores are separated by Inter-ring Sulphonamide Groups

Y. P. Berkman and M. L. Shevchenko
Nauch. Zapiski L'vov. Politekh. Inst., Ser. Khim.-Tekhnol., 50, (3), 89–98 (1958); *Chem. Abs.*, 53, 17515 (25 Sept 1959)

O₂NZCl and p-C₆H₄(NH₂)₂ (X, Y, and Z = o-, m-, and p-C₆H₄SO₂ respectively) form p-(O₂NZNH)₂C₆H₄ reduced by aq. Na₂S to p-(H₂NZNH)₂C₆H₄. m-(O₂NYNH)₂C₆H₄, m-(H₂NYNH)₂C₆H₄, o-(O₂NXNH)₂C₆H₄, and o-(H₂NXNH)₂C₆H₄ were similarly prepared. The o-diamine was only slightly soluble in boiling HCl but the other two diamines were soluble. These diamines were condensed with the corresponding O₂NC₆H₄SO₂Cl and reduced to yield the p-, m-, or o-5-benzene ring dinitro compounds. Dyes formed by diazotising these amines increased in fastness as the number of rings increased. C.O.C.

Polysulphonamide Diazo Components for Benzidine Azo Dyes

M. L. Shevchenko and Y. P. Berkman
Nauch. Zapiski L'vov. Politekh. Inst., Ser. Khim.-Tekhnol., 50, (3), 97–100 (1958); *Chem. Abs.*, 53, 17515 (25 Sept 1959)

The following compounds were prepared by using p-(C₆H₄NH₂)₂ according to the methods described in the preceding abstracts: p-(CH₃CONHZNHC₆H₄)₂, p-(O₂NYNHNC₆H₄)₂, p-(CH₃CONHZNHNHC₆H₄)₂, p-(O₂NYNHYNHNC₆H₄)₂ and their corresponding diamines. The last two diamines are less soluble in acid and harder to diazotise than the first two. C.O.C.

Azo Dyes having Sulphonil Ester Groupings

L. E. Lukavskaya and Y. P. Berkman
Nauch. Zapiski L'vov. Politekh. Inst., Ser. Khim.-Tekhnol., 50, (3), 102–109 (1958); *Chem. Abs.*, 53, 17515 (25 Sept 1959)

The diazonium salt of H₂N(C₆H₄SO₂)_nONH₂ is obtained as a precipitate if an aqueous solution of the amine is heated with NaNO₂ dissolved in 10% H₂SO₄ for 3–4 hr. at 30–35°C. and then cooled. These diazonium salts are unusually stable, decomposing at the following temperatures (n and temperature given): 1, 123–128°C.; 2, 145–156°C.; 3, 165–170°C.; 4, 176–181°C. They were coupled with 2,6-naphtholsulphonic acid to yield Acid Orange n-SE (SE = sulphonyl ester), with 1,4-H₂NC₆H₄SO₃H to yield Acid Red n-SE and with 2-C₁₀H₇OH to yield Orange n-SE. Dyes where n = 3 or 4 had satisfactory fastness. C.O.C.

Azo Dyes containing Different Proportions of Sulphonamide and Sulphonic Ester Groups

L. E. Lukavskaya *Nauch. Zapiski L'vov. Politekh. Inst., Ser. Khim.-Tekhnol.*, 50, (3), 110–118 (1958); *Chem. Abs.*, 53, 17515 (25 Sept 1959)

H(HNY)_m(OZ)_nOH (m + n = 4); Y and Z = m- and p-C₆H₄SO₂ respectively) was prepared and coupled with 2,6-naphtholsulphonic acid. The resulting dyes had all the same fastness. Apparently an SO₃ link is equivalent to an SO₂NH link. C.O.C.

Polysulphonamide Diazo Components of Azo Dyes having a Nitro Group in the End Ring

M. L. Shevchenko *Nauch. Zapiski L'vov. Politekh. Inst., Ser. Khim.-Tekhnol.*, 50, (3), 119–125 (1958); *Chem. Abs.*, 53, 17515 (25 Sept 1959)

(CH₃NHZNH)₂C₆H₄NO₂ (Z = p-C₆H₄SO₂), p-[CH₃CO-NH(ZNH)₂]₂C₆H₄NO₂, p-[CH₃CONH(ZNH)₂]₂C₆H₄NO₂, and p-[CH₃CONH(ZNH)₂]₂C₆H₄NO₂ were prepared by the

methods described in the preceding abstracts. Their properties and those of the free amines are given.

C.O.C.

Electronic Structure and Physicochemical Properties of Azo-compounds

V—Influence of Substituents on the Absorption Spectrum of Phenylazazulene, a Contribution towards knowledge of the Plattner Displacement Rule

F. Gerson and E. Heilbronner

Helv. chim. Acta, **42**, 1877–1908 (15 Oct 1959)

The MO-theoretical data calculated in IV when applied to the experimental results of I, II, and III, show that for phenylazazulenes substituted in the benzene nucleus: (1) the position $\bar{\nu}_{B.I}$ of the band corresponding to the long-wave transition depends linearly on the Hammett σ_x value of the substituent x , and (2) the shift $\Delta\bar{\nu}_{B.II}$ of the intense $\pi \rightarrow \pi^*$ transition at 24,000 cm^{-1} on protonation of the azo link depends linearly on σ_x provided that $\sigma_x - \sigma_x'$ is negative. These results provide experimental verification of a prediction based on a generalisation of Plattner's rules (cf. *Helv. chim. Acta*, **24**, 283 E (1941)). The $\Delta p K'$ -values (on an H_0' -scale) in the system ethanol, water/hydrochloric acid are given for 23 deriv. of phenylazazulene, and the course of the stepwise protonation of *p*-dimethylaminophenylazazulene is discussed.

VI—Relative Basicities of Arylazazulenes in the Systems Ethanol/Hydrochloric Acid and Methylisobutylketone/Sulphuric Acid

A. Mörikofer and E. Heilbronner

Ibid., 1909–1916

The relative basicities and the spectral shift of the band II on protonation of 29 azazulenes are recorded for the system methylisobutylketone/sulphuric acid, and compared with the data of V for the system ethanol/hydrochloric acid. The data are found to be largely independent of the solvent system, and so may be correlated with characteristic values obtained from molecular orbital models.

H.H.H.

Absorption Spectra of Dyes

II—Fading of Copper Complexes of Direct Dyes

Y. Ishii *J. Soc. Textile Cellulose Ind. Japan*, **15**, 56–61

(Jan 1959)

Viscose films are dyed by, e.g. Benzo Azurine G (C.I. Direct Blue 8), Chlorazol Sky Blue FF (C.I. Direct Blue 1), and by their copper complexes. Changes in absorption spectra produced by exposure in a Fade-Ometer for different intervals of time (up to 127 hr.) are given and indicate that the optical densities of the normal dyes decrease about 50% before 127 hr. whereas the copper complexes show only 10–20% reduction. When the dyed films are treated in 1% aq. CuSO_4 the light fastness of each normal dye is increased but that of the complex dye is unaffected.

L.P.

Absorption Spectra of Dyes

III—Complexes in Mixtures of Chlorazol Sky Blue FF (C.I. Direct Blue 1) and *p*-Nitroaniline- γ -Acid in Aqueous Solution

T. Koboyashi, Y. Tanazaki, and N. Ando

Bull. Chem. Soc. Japan, **32**, 675–679 (July 1959)

The absorption spectra of mixed solutions of Chlorazol Sky Blue FF with *p*-nitroaniline- γ -acid (coupled with respect to either $-\text{NH}_2$ or $-\text{OH}$) are non-additive, particularly at ca. 620 $\text{m}\mu$. The observed changes in optical density at this wavelength with variation in the composition of the mixtures are explained in terms of the formation of a 1:1 complex when the concentration of the acid dye is low compared with that of Sky Blue FF and of higher complexes in the presence of excess of acid dye.

IV—Mixtures of Chlorazol Sky Blue FF (C.I. Direct Blue 1) and Dyes from Sulphanilic Acid and Cresidine

T. Koboyashi, Y. Tanazaki, and N. Ando

Ibid., 680–684

The absorption spectra of mixed solutions of Sky Blue FF and sulphanilic acid-cresidine (SC_1) are additive when the ratio of the two dyes is ca. 1:5, but not at 1:40. The non-additive spectra pass through an isobestic point at 650 $\text{m}\mu$. (SC_1 not absorbing) indicating formation of a definite complex. Mixtures of Sky Blue and SC_1 -cresidine (SC_2) give non-additive spectra at all ratios, which can be explained in terms of a 1:1 complex.

A.J.

Separation, Estimation, Orientation, and Ultraviolet Spectra of Isomeric Azo Compounds formed by Diazo Coupling to 1-Naphthylamine and its Derivatives

E. R. Ward, B. D. Pearson, and P. R. Wells

J.S.D.C., **75**, 484–486 (Oct 1959)

Mechanism of Reduction of Azo Compounds by Phenyl Hydrazine using labelled Nitrogen

B. A. Geller *Ukrain. khim. zhur.*, **25**, 196–198 (May 1959)

The reduction of azobenzene (I) and *p,p'*-azotoluene with phenylhydrazine (II) containing ^{15}N has been studied. It is shown that the liberated nitrogen is provided by I and that ^{15}N from II does not enter the hydroazo compound. The mechanism of reduction is probably based on the formation of a cyclic intermediate complex between I and II involving hydrogen bonding.

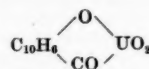
G.J.K.

Uranyl Chelate Complex of 1-Hydroxy-2-Naphthoic Acid

S. C. Tripathi and S. Prakash

J. Indian Chem. Soc., **36**, 19–22 (Jan 1959)

1-Hydroxy-2-naphthoic acid gives with uranyl ions a 1:1 complex—



having an apparent instability constant K of $2.42 \pm 0.5 \times 10^{-2}$.

C.H.R.

Coupling of Weakly Reactive Diazo Compounds with Azotols

R. M. Shchegoleva and F. I. Sadov

Tekstil. prom., **19**, 62–64 (July 1959)

The coupling reaction of weakly reactive diazo components with "Azotols" (azoic coupling components) is investigated, and maximum yields of pigment are obtained within a very narrow pH range (10.5–11). The reactivity of the Azotols diminishes in the series: $\text{PA} > \text{OA} > \text{A} > \text{MNA}$.

G.J.K.

π -Electronic Structures of α -Naphthoquinone and Anthraquinone

A. Kuboyama

Bull. Chem. Soc. Japan, **31**, 752–756 (Sept 1958)

Anthraquinone Derivatives. XXVII—Hydrolysis of 1,5- and 1,8-Nitrosulphonic Acids of Anthraquinone

V. V. Kozlov

Zhur. obshch. khim., **29**, 1344–1349 (April 1959)

The hydrolysis of 1,5-(I), and 1,8-(II) anthraquinone-nitrosulphonic acids in water in a sealed system has led to the formation of 1,5- and 1,8-nitrohydroxyanthraquinones. Hydrolysis in conc. H_2SO_4 in open and closed systems is complicated by redox reactions. The presence of the nitro group in I, and particularly II, strongly reduces the mobility of the sulphonic acid group.

G.J.K.

Polarographic Study of Anthraquinone Compounds and their Tetra- and Octa-hydro Derivatives

V. E. Ditsent

Zhur. obshch. khim., **29**, 1370–1374 (April 1959)

The reduction of 12 anthraquinone (A) deriv., using the dropping mercury electrode, has been investigated. It is shown that the introduction of methyl, ethyl, or propyl groups into the molecule of A and its hydro-derivatives does not affect the half-wave potential, whereas hydrogenation of side rings in A leads to a shift of the half-wave potential of 0.12–0.15 V for tetrahydro and 0.20–0.23 V for octahydro deriv.

G.J.K.

Hydroxy Derivatives of Anthracene. IV—1-Nitroso-2-anthrole-4-sulphonic Acid and 2-Nitroso-1-anthrole-4-sulphonic Acid

S. V. Bogdanov and M. V. Gorelik

Zhur. obshch. khim., **29**, 1225–1229 (April 1959)

2-Nitroso-1-anthrole-4-sulphonic acid (I) has been prepared by action of HCl on the bisulphite cpd. of 1,2-anthraquinone dioxime or 1,2-anthraquinone dioxime-4-sulphonic acid, and through action of hydroxylamine and HCl on the bisulphite cpd. of 1-nitroso-2-anthrole or 1,2-anthraquinone-4-sulphonic acid. The chemical behaviour towards alkalis, aromatic amines, and nitric acid has been investigated. 1-Nitroso-2-anthrole-4-sulphonic acid (II) has been prepared by nitrosation of 2-anthrole-4-sulphonic acid. The chelating properties of I and II with iron and cobalt are compared.

G.J.K.

Benzdithiylum Dyes—II

L. Soder and R. Wizinger

Helv. chim. Acta, **42**, 1779–1785 (15 Oct 1959)

Starting from toluene dithiol, the syntheses of six 2-arylbendithiylum dyes are described viz., (I) 1,5-methyl-2-phenyl-, (II) 5-methyl-2-[4-methoxyphenyl]-, (III) 5-methyl-2-[4-dimethylaminophenyl]-, (IV) 5-methyl-2-styryl-, (V) 5-methyl-2-[4-methoxystyryl]-, and (VI) 5-methyl-2-[4-dimethylaminostyryl]-1,3-benzdithiylum-perchlorate. In the cases of (VI) and its vinylene homologue, [2-(5-methyl-1,3-benzdithiylum)]-[1-(4-dimethylaminophenyl)]-tetramethincyanin-perchlorate (prepared by condensing with dimethylamino-cinnamic aldehyde), the so-called mean value rule for the absorption max. of an unsymmetrical cyanine appears to be invalid, and this problem is discussed. H.H.H.

Acid Dyes

G. Cordella

Ricerca sci., **28**, 2271–2273 (1958)*Chem. Abs.*, **53**, 17517 (25 Sept 1959)

2-(p-Aminophenyl)-benzotriazole (I) (1 g.) was diazotized at room temperature, neutralised with NaHCO₃ and added to a cold alkaline solution of R acid (1.6 g.). After standing overnight, the dye was salted out with 20% NaCl, filtered off, boiled in aq. Na₂CO₃ with C, filtered, salted out hot, and finally purified through the Ba salt. I, I-1-oxide and 1-methyl-2-(p-aminophenyl)-benzimidazole were similarly coupled with R acid, H acid, and chromotropic acid. Red dyes were obtained with R acid, the others were violets. C.O.C.

Photoreduction of Acridine Dyes

F. Millich

Univ. Microfilms (Ann. Arbor, Mich.),

L.C. Card No. Mic 59–1774, 856 pp.:

Dissertation Abs., **19**, 3148–3149 (1959);*Chem. Abs.*, **53**, 17513 (25 Sept 1959)**Colourless Additive Compounds from Triphenylmethane Dyes and Triphenylphosphine**

O. Neunhoeffer and W. Weigel

Naturwissenschaften, **43**, 447 (1956);*Chem. Abs.*, **53**, 17516 (25 Sept 1959)

Use of suitable solvents and excess of (C₆H₅)₃P stabilised the carbenium boundary state with a positive charge and an electron sextet at the central C atom. Formation of the additive compound was accompanied by loss of colour, the rate of which increased with temperature. This loss of colour was possible with Malachite Green (C.I. Basic Green 4) oxalate, and with Fuchsin (C.I. Basic Violet 14), Crystal Violet (C.I. Basic Violet 3), and Methyl Violet (C.I. Basic Violet 1) chlorides, in dioxane, tetrahydrofuran, CHCl₃, C₆H₅NO₂, and pyridine. Loss of colour could not be effected in alcohol. C.O.C.

Reaction of Rhenium with Methyl Violet (C.I. Basic Violet 1). II—Reactions of Methyl Violet with Elements associated with Rhenium

A. T. Pilipenko and V. A. Obolonechik

Ukrain. khim. zhur., **25**, 358–362 (June 1959)

The reactivity of Methyl Violet with elements naturally occurring in rhenium-containing ores and with several anions has been investigated, and the results are tabulated giving optimum pH range, extractability in toluene, masking of interfering radicals by complex formation. Methyl Violet is recommended as a highly specific reagent for rhenium. G.J.K.

Formation of the Stable Semiquinone of Methylene Blue (C.I. 52015) by Irradiation with Visible Light and γ-rays

M. Koizumi and H. Obata

Bull. Chem. Soc. Japan, **31**, 823–827 (Oct 1958)

When Methylene Blue in 22.9 N-H₂SO₄ containing a little alcohol or benzoic acid, is exposed to either γ-rays or visible light *in vacuo* it is reduced to a stable semiquinone. In absence of alcohol or benzoic acid formation of a semiquinone or irreversible decomposition of the dyes scarcely ever takes place *in vacuo* while in an aerated solution the only reaction is the irreversible decomposition of the dye. C.O.C.

Irreversible Photobleaching of Solutions of Fluorescent Dyes. VI—Photobleaching of Uranine (C.I. 45350) in Alkaline Solution

M. Imamura

Bull. Chem. Soc. Japan, **31**, 962–969 (Nov 1958)**Pressure and Temperature Effects on the Kinetics of the Alkaline Fading of Organic Dyes in Aqueous Solution**

D. T. Y. Chen and K. J. Laidler

Can. J. Chem., **37**, 599–612 (1959)*Chem. Abs.*, **53**, 17515 (25 Sept 1959)

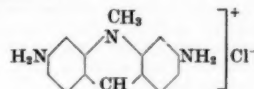
A study of the kinetics of fading reactions involving attack by an OH⁻ on a large organic dye molecule (Bromophenol Blue, Phenolphthalein, Crystal Violet (C.I. Basic Violet 3), and Malachite Green (C.I. Basic Green 4)). The effects of pressure caused by electrostriction of the solvent around ions and dipoles and caused by structure are separated and discussed. With Bromophenol Blue, Phenolphthalein, and Malachite Green the quinoid form of the dyes is structurally somewhat larger (relative to the carbinol forms) than with Crystal Violet, so that fading involves decrease in volume. With Bromophenol Blue and Phenolphthalein electrostriction effects contribute slightly but these are negligible for Malachite Green and Crystal Violet. C.O.C.

Absorption Spectra of Dye Films *in Vacuo*

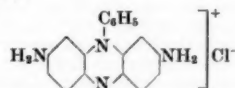
L. A. Lyzina and A. T. Vartanian

Optika i Spektroskopiia, **6** (Feb 1959)*Optics and Spectroscopy* (English translation),**6**, 110–114 (Feb 1959)

Preparation of solid dye films by sublimation is described together with measurement of their absorption spectra *in vacuo*. Absorption curves of the following dyes are given: Fuchsine (C.I. Basic Violet 14), Crystal Violet (C.I. Basic Violet 3), Rhoduline Orange (C.I. Basic Orange 14), Trypaflavine—



Phenosafranine—



Safranin O (C.I. Basic Red 2), Pyronine G (C.I. 45005), Rhodamine B (C.I. Basic Violet 10), Rhodamine 6G (C.I. Basic Red 1), Auramine O (C.I. Basic Yellow 2), Thionine (C.I. 52000), and Methylene Blue (C.I. Basic Blue 9). These curves are compared with those obtained from solutions and films obtained by deposition from solution. C.O.C.

Noncrystallising Mixed Phthalocyanine Pigments

Y. Bansho, T. Yagi, S. Suzuki, and G. Imura

Kogyō Kagaku Zasshi, **61**, 92–94 (1958)*Chem. Abs.*, **53**, 17531 (25 Sept 1959)

Various phthalocyanine (C.I. 74100) salts (Sn, Zn, Fe, Al, Mg, Co, Pb, Ni, Cr, and Ti) were mixed in various proportions (2–20%) with Cu phthalocyanine (C.I. 74160) and sulphonated to yield mixed pigments. The tendency of Cu-phthalocyanine to crystallise in xylene is reduced by addition of Fe-, Al-, Ti-, Sn-, and Mg-phthalocyanines. The fastness to light of Cu-phthalocyanine is reduced by addition of Fe-, Al-, Sn-, Mg-, and Cr-phthalocyanines. The spectrum shifts to the longer wavelengths by addition of Fe-, Al-, Ti-, Ni-, and Cr-phthalocyanines. The testing strength of ZnO (C.I. Pigment White 4)-Cu-phthalocyanine paints tends to decrease when other phthalocyanine salts are present except for the Zn and Fe salts which have no effect; the reduction is rather noticeable when Al-, Co-, Ti-, and Cr-phthalocyanines are present. C.O.C.

Anomalous Spectrophotometric Behaviour of Copper Phthalocyanine-Benzidine Yellow (C.I. Pigment Blue 15—C.I. Pigment Yellow 12) Mixtures

A. Di Bernardo and P. Resnick

J. Opt. Soc. Am., **49**, 480–484 (May 1959)

Spectrophotometric reflectance curves of mixtures of dispersed copper phthalocyanine and Benzidine Yellow differed radically from those expected of a combination of the two pigments. Preliminary tests indicated that some kind of interaction occurred between them. Microscopic examination shows it was not flocculation and other tests showed it could not be crystal transformation of the

phthalocyanine. It is probably caused by the Benzidine Yellow exerting a solvation effect on the copper phthalocyanine.

Action of Reducing Agents on Copper Phthalocyanine and its Chlorinated Derivatives

M. Shigemitsu

Bull. Chem. Soc. Japan, **32**, 592-505 (May 1959)

Finely divided samples of chlorinated phthalocyanines darken when treated with sulphonylate-formaldehyde. This is accompanied by slight decreases in chlorine content but not by significant change in particle size distribution. Apparently change of chemical composition occurs during the reduction.

A.J.

Synthesis of Chlorinated Copper Phthalocyanines from Chlorophthalic Anhydrides

M. Shigemitsu

Bull. Chem. Soc. Japan, **32**, 691-693 (July 1959)

Eight chlorinated copper phthalocyanines were prepared from 3- and 4-monochloro, 3,4-, 3,6- and 4,5-dichloro, 3,4,6- and 3,4,5-trichloro and 3,4,5,6-tetrachlorophthalic anhydride (I) by condensing each in turn with cuprous chloride and urea. All except I yielded the expected chlorinated copper phthalocyanine but in lower yield than the unchlorinated compound. I yielded a copper phthalocyanine containing 12 rather than 16 chlorine atoms. There was evidence that chlorine in position 6 is lost.

A.J.

Cyanine Dyes from 4-Methylcinnoiline

A. B. Lal

J. Indian Chem. Soc., **36**, 64 (Jan 1959)

4-Methylcinnoiline methiodide and 4-anilinoethyl cinnoiline methiodide have been condensed with *p*-(dimethyl-amino)benzaldehyde and ethylorthoformate and with lepidine methiodide and quinaldine ethiodide respectively to give three corresponding cyanine dyes, the properties of which are not described.

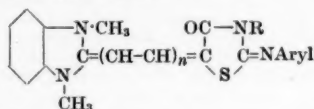
C.H.R.

Merocyanines derived from Benzimidazole

P. K. Misra, B. K. Patnaik, and M. K. Rout

J. Indian Chem. Soc., **36**, 35-40 (Jan 1959)

2-Methyl-*N*-methylbenzimidazole methiodide has been condensed with diphenylformamidine, *B* anilinoacrolein-anilhydrochloride and glutaric aldehyde dianilide hydrochloride and the resulting products condensed thiazolidones to give the dye—



(*n* = 1, 2 or 3; R = H or Ar).

C.H.R.

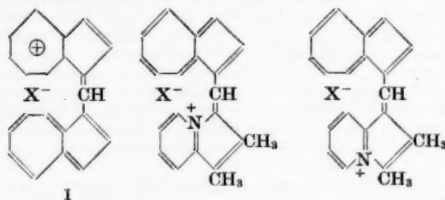
Azulene Polymethine Dyes

F. N. Stepanov and N. A. Aldanova

Angew. Chem., **71**, 125 (1959)

Chem. Abs., **53**, 17516 (25 Sept 1959)

Analogy between indolizine and azulene dyes led to synthesis of I (λ_{\max} 617 m μ in ethanol) from azulene-1-aldehyde (II) and of the mixed dyes III (λ_{\max} 580 m μ) and IV (λ_{\max} 568 m μ) from II and indolizines.



(X = Cl, ClO₄ or BF₄).

C.O.C.

Ageing of Sulphur Dyes

R. M. Sheftel' and I. L. Khmel'nitskaya

Tekstil. prom., **19**, 46-48 (June 1959)

Thin layers of sulphur dyestuffs were subjected to accelerated ageing under controlled conditions, and their dyeing properties compared with identical fresh dyestuff. The following series of decreasing stability is put forward: browns, blues, greens, blacks.

G.J.K.

Mechanism of Photoreduction of Xanthene Dyes

V. F. Tsepalov and V. Ya. Shlyapintokh

Izvestiya Akad. Nauk S.S.S.R., otdel. khim. nauk, **637-643** (April 1959)

The photoreduction of eosin, erythrosin, and Rose Bengal with ascorbic acid (and butyric aldehyde) in pyridine (and ethanol) has been investigated. Measurements of the absorption spectra (visible and ultraviolet) and kinetic measurements of the redox potentials indicate the formation of semiquinones of the above dyes. A mechanism of photoreduction is suggested and the constants for the rate of reduction (eosin semiquinone) are evaluated.

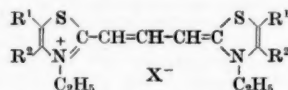
G.J.K.

Thiazole Carbocyanines with Aryl Groups in Thiazole Nuclei. VI—Effect of the Nitro Group on the Colour of Thiazole Carbocyanines

E. D. Sých

Ukrain. khim. zhur., **25**, 344-347 (June 1959)

Derivatives of thiazole carbocyanines of general formula—



(R¹ = H, NO₂, C₆H₅, *p*-O₂N-C₆H₄, C₆H₅-C₆H₄, or *p*-O₂N-C₆H₅-C₆H₄; R² = H or CH₃) have been prepared and the absorption max. (visible spectrum) shown. The effect of the NO₂ group on the colour is weakened by the introduction of aryl groups between the NO₂ group and the thiazole nucleus.

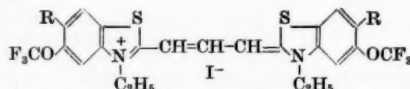
G.J.K.

Cyanine Dyes Containing Fluorine. VI—Synthesis of Cyanine Dyes from 5-Trifluoromethoxy-6-acetylaminobenzothiazole

L. M. Yagupol'skii

Zhur. obshch. khim., **29**, 1312-1315 (April 1959)

Quaternary salts of six cyanine dyes of the general form—



where R = H, Cl, I, SCH₃, NHCOCH₃, or NH₂, have been prepared, and their absorption max. found to be almost identical with those of the corresponding methoxy deriv.

G.J.K.

Remazol (FH) Colours: a Chemically new System of Reactive Dyes

E. F. Sommer

Amer. Dyestuff Rep., **47**, 895-899 (15 Dec 1958)

A brief survey of the history of reactive dyes and an account of the constitutions of those obtained by use of cyanuric chloride is followed by an account of the Remazol dyes which are of formula Dye-SO₂-CHR¹-CR²-R³-OZ (Z = SO₂H or the like). Their typical reactive group is -SO₂-CH₂-CH₂-O-SO₂H which reacts very quickly with cellulose in presence of alkali to form an ether linkage Dye-SO₂-CH₂-CH₂-O-cellulose. Their use in dyeing and printing cotton is described.

C.O.C.

Photoreduction of Dyes in Rigid Media. II—Photo-redox Properties of Thiazine Dyes

B. Broyde and G. Oster

J. Amer. Chem. Soc., **81**, 5099-5103 (5 Oct 1959)

Thiazine dyes are photoreduced to the leuco dyes when incorporated in high viscosity glasses of polyhydroxy compounds. The rate of reduction is proportional to the square root of the diffusion coefficient. This suggests a diffusion-controlled process in which stationary state conditions are not achieved. Illumination of highly concentrated dye glasses containing an added mild reducing agent yields an intermediate colour which reverts to the original dye on softening the glass. This species is an entrapped dimer of the normal dye. Near ultraviolet irradiation of the leuco dye glass yields the normal dye and other coloured species. In acid glass a red form is produced and in basic glasses a yellow form, both these revert to the leuco dye on the glasses being softened. The ratio of red to blue forms increases as the viscosity of the medium increases. These intermediate species are believed to be a semiquinone and a diradical, or a molecule in the triplet state trapped in the rigid medium.

C.O.C.

Dye-sensitised Photo-oxidation

G. Oster, J. S. Bellin, R. W. Kimball, and M. E. Schrader
J. Amer. Chem. Soc., **81**, 5095-5099 (5 Oct 1959)

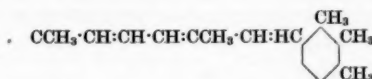
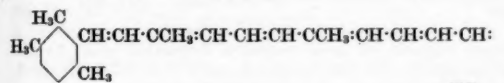
Only dyes capable of being photoreduced can act as sensitizers for photo-oxidation. Both reactions proceed through a metastable long-lived excited state of the dye. Kinetic study using proflavine as the sensitizer on *p*-toluenediamine as the substrate shows that the dye molecule in the long-lived state reacts with oxygen or forms a labile peroxide which in turn oxidises the substrate. The quantum yield of the reaction decreases markedly with increasing dye concentration because of concentration quenching of the long-lived state and the peroxide. The large limiting quantum yield achieved, viz. 3.0, is attributable to formation of a polymer of the oxidised aromatic amine. C.O.C.

Renieratene, a Carotenoid containing Benzene Rings, isolated from a Sea Sponge

M. Yamaguchi

Bull. Chem. Soc. Japan, **31**, 739-742 (Sept 1958)

Evidence which indicates that renieratene, $C_{10}H_{48}$, is a new type of carotenoid—



C.O.C.

Photochemical and Stereochemical Properties of Carotenoids at Low Temperatures**(1) Photochemical Behaviour of Retinene**

L. Jurkowitz *Nature*, **184**, 614-617 (22 Aug 1959)

(2) Cis-trans Isomerism and Steric Hindrance

J. N. Loeb, P. K. Brown, and G. Wald
Ibid., 617-620

(3) Discussion

G. Wald *Ibid.*, 620-624

Studies on Haematoxylin and Haematein, the Colouring Principles of Logwood (C.I. Natural Black 1)

G. C. Lalor and S. L. Martin

I—Absorption Spectra of Pure Compounds in Various Solvents and a Spectrophotometric Method of Analysis for Haematoxylin and Haematein

J.S.D.C., **75**, 513-517 (Nov 1959)

II—Behaviour in Aqueous Solutions at Varying pH, and the pK Values

Ibid., 517-521

"Dye Balls" and "Family Colors". The Story of Packaged Dyes for the Home

S. M. Edelstein

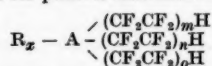
Amer. Dyestuff Rep., **48**, 32-36 (27 July 1959)

PATENTS**Aromatic Intermediates Containing Fluorinated Side-chains**

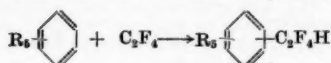
FH

BP 822,009

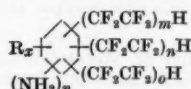
Intermediates for producing dyes of excellent fastness properties or for plastics and insecticides are of formula—



(A = benzene, naphthalene or trinuclear residue; R = H, Alk, aryl, ether, thioether, COOH, carboxylic ester or amide, NH_2 , SO_3H , sulphonic acid ester or amide, Hal, OH, SH quinone O atom, phosphonic acid group or NO_2 ; $x = 3$ when A is benzene, 5 when A is naphthalene, 7 when A is trinuclear; $m = < 1$; n and $o = < 9$). These compounds are formed by reaction between the aromatic starting material and tetrafluoroethylene under pressure at 100-200°C. in presence of a cobalt carbonyl, e.g.—



The catalyst, e.g. $(\text{Co}(\text{CO})_2)_2$ or $(\text{Co}(\text{CO})_2)_4$, may be dissolved in the aromatic compound; or Co or a Co compound may be used along with sufficient carbon monoxide to give 20-50 atm. pressure. Individual products are obtained from the reaction mixture by fractional distillation or fractional crystallisation. Physical and chemical properties of some of the products are discussed, e.g. because of the stability of the $-\text{C}_2\text{F}_4\text{H}$ group, nitration and reduction will yield amino derivatives—



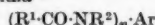
which may be diazotised and coupled with suitable end-components to give dyes of excellent fastness. E.T.

Opalescent Pigments for incorporation in Detergents

Gillette Co.

USP 2,891,912

Amides of formula—



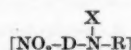
(R^1 = aliphatic hydrocarbon of 1-23 C; R^2 = H or aliphatic hydrocarbon of 1-10 C; $n = 1$ or 2; Ar = subst. or unsubst. aromatic), e.g. palmitic *p*-aniside, when added to detergents impart an opalescent appearance. They do not settle out even after long standing. C.O.C.

Nitro Reactive Dyes

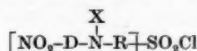
ICI

BP 821,963

Yellow nitro dyes which form chemical links with protein, cellulosic or polyamide fibres when applied in conjunction with an acid-binding agent are of formula—



(D = benzene or naphthalene nucleus; N = nitrogen atom ortho to the NO_2 group; X = H, Alk or subst. Alk; R = non-aryl organic radical attached to N through a C atom and which may join with X or D in the other *o*-position to N to form a heterocyclic radical; R also contains a β -halogeno-alkyl-sulphamyl group). They are made by condensing a β -halogeno-alkylamine with—



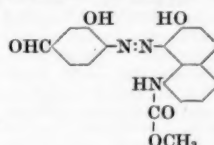
in aq. or aq. organic medium generally at < 30°C. in presence of an acid-binding agent. The dyes containing SO_3H groups are especially suitable for cellulosic materials. E.T.

Metallisable and Metal-complex Monoazo Dyes for Wool from o-Aminohydroxybenzaldehydes

Gy

BP 822,734

3-Hydroxy-4-aminobenzaldehyde (I) and its derivatives, diazotised and coupled with *o*-coupling hydroxy and amino-compounds, give monoazo compounds which may be metallised in substance or on the fibre. Particularly valuable are the 1:2 Cr- or Co-complexes of such monoazo compounds free of SO_3H groups using 1-acylamino-7-naphthols as coupling components, which dye wool grey from a neutral or weakly acid bath; the aldehyde group confers the desired degree of water-solubility on these metal-complexes. Thus diazotised I is alkali-coupled with 1-carbomethoxyamino-7-naphthol to give—



Boiling with aq. sodium chromosalicylate gives the Cr complex. E.S.

Azo Disperse Dyes having a Pyrimidine Ring

ICI

BP 822,948

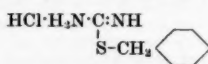
Aminoazo compounds free of SO_3H and COOH groups are condensed with chloropyrimidines, e.g. 2,4,6-trichloro- or 2,4-dichloro-6-methyl-5-nitro-pyrimidine to give yellow, orange, red, violet, and blue disperse dyes for cellulose

acetate and nylon. The same dyes can be made by coupling suitable diazo compounds with coupling components made by condensing an amino compound with suitable chloropyrimidines. Thus 4-amino-2'-hydroxy-5'-methylazobenzene in ethanol is condensed with 2,4,6-trichloropyrimidine in presence of Na_2CO_3 to give a yellow, and diazotised 4-amino-3-chlorobenzenesulphonamide is coupled with the condensation product of 1 mol. of 2,4-dichloro-6-methyl-5-nitropyrimidine with 1 mol. of *m*-amino-*NN*-bis- β -hydroxyethylaniline to give a red for nylon.

E.S.

Isothiuronium Salts of Metal(Chromium)-complex Monoazo Dyes—Colorants for Lacquers and Synthetic Polymers

Ciba BP 820,626
Chromium-complexes, especially 1:1 complexes containing an SO_3H group, are made into isothiuronium salts, using preferably *S*-alkyl (or benzyl)isothiuronium chlorides to give pigments or transparent colorants for lacquers and spinning solutions of synthetic polymers, e.g. cellulose acetate. Thus benzyl chloride is condensed with thiourea to give *S*-benzylisothiuronium chloride—

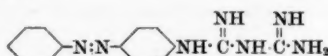


An aq. solution of this is run into a solution of the 1:1 Cr-complex of the monoazo compound 1-amino-2-naphthol-4-sulphonic acid \rightarrow 1-naphthol-8-sulphonic acid (C.I. 14880). The precipitated salt dissolves in alcohol and in cellulose nitrate lacquers with a blue colour.

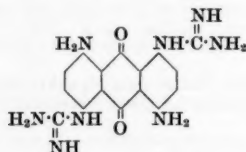
E.S.

Basic Monoazo and Anthraquinone Dyes for Polyacrylonitrile Fibres, having Guanidyl Groups

FBy BP 822,961
The salts of guanidyl or biguanidyl derivatives of suitable monoazo and anthraquinone compounds are soluble in water in the form of their salts, and dye polyacrylonitrile fibres yellow, orange, red, and blue from acid baths. Thus—



is a reddish yellow, and



is a blue.

E.S.

Yellow Metal(Chromium)-complex Monoazo Pyrazolone Dyes for Wool, Nylon, etc.

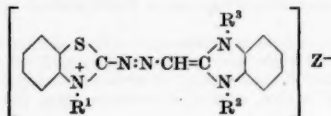
BASF BP 823,393
Halogenoanthranilic acids are diazotised and coupled with pyrazolones free of COOH , SO_3H , and SO_2NH_2 groups and the monoazo compounds heated with Cr compounds to give complexes which are greener yellows than the similar compounds without halogen atoms. They dye wool, nylon, etc., from neutral or weakly acid baths, and are suitable also as colorants for lacquers and fibre spinning solutions. Thus diazotised 4-chloroanthranilic acid is coupled with 3-methyl-1-phenyl-5-pyrazolone, and the monoazo compound so formed is stirred at 110°C. with chromium formate in formamide.

E.S.

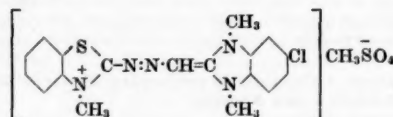
Yellow Fluorescent Basic Diazocyanine Dyes

BASF BP 821,001

The title dyes of formula—



(R^1 and R^2 = Alk, cycloalkyl, aralkyl or Ar of < 11 C; R^3 = Alk, cycloalkyl, or aralkyl of < 11 C; the benzene nuclei may contain Hal, Alk, OAlk, SO_2NH_2 , etc., substituents; Z^- = an inorganic or organic anion) are prepared by condensing suitable benzthiazolone-(2)-hydrazones with benzimidazole derivatives, followed by treatment with alkylating, etc., agents to give the quaternary ammonium compounds. Thus 3-methylbenzthiazolone-(2)-hydrazone and 5-chlorobenzimidazole-2-aldehyde are stirred at 80°C. in dimethyl formamide for 1 hr. Dimethyl sulphate is then added and heating continued at 120°C. The product—

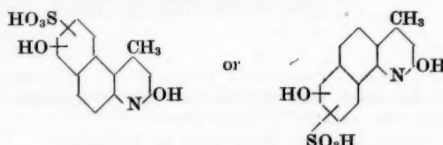


gives a pure yellow aqueous solution, unchanged in hue by addition of ammonia or dil. HCl.

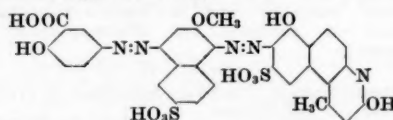
E.S.

Copperable Disazo Direct Dyes

Gy BP 822,096
Suitable aminomonoazo compounds, containing a group capable of metal-complex formation *ortho* to the amino group, are diazotised and coupled with 2-hydroxy-4-methyl (*m*-hydroxysulphobenzoyl)quinolines—



(the OH and SO_3H groups are in *meta*-position to each other) to give direct dyes—olives, greys, blues, and greens—which may be coppered in substance or on the fibre. Or a suitable diamine (e.g. dianisidine) may be tetrazotised and coupled with 1 mol. of such a quinoline derivative and 1 mol. of a naphtholsulphonic acid, etc. Thus the aminoazo compound 5-aminosalicylic acid \rightarrow 2-methoxy-1-naphthylamine-6-sulphonic acid is diazotised and coupled with an alkaline solution of 2-hydroxy-4-methyl-5,6-(3'-hydroxybenzoyl)quinoline-5'-sulphonic acid in presence of pyridine to give—



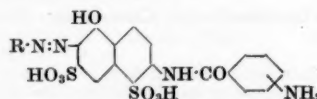
which dyes cellulose blue-grey improved in fastness to light and washing by aftercoppering.

E.S.

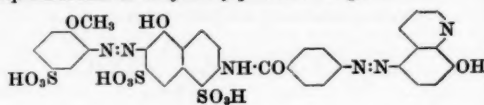
Red Metallisable Disazo Direct Dyes

Ciba BP 821,331

Aminomonoazo compounds—



(R = aryl of benzene or naphthalene series, preferably having a group capable of metal-complex formation *ortho* to the azo group) are diazotised and coupled with 8-hydroxyquinoline to give the title dyes, which may be metallised (especially with Cu) in substance or on the fibre, and give reds of good brightness. Thus 2-aminoanisole-4-sulphonic acid is diazotised and coupled in presence of Na_2CO_3 with 2-(*p*-aminobenzoylamino)-5-naphthol-1,7-disulphonic acid. The aminomonoazo compound so formed is then diazotised and coupled with a solution in aq. ammonia of 8-hydroxyquinoline to give—



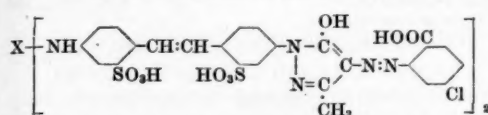
11 C;
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methyl
120°C.

which dyes cellulose bright red rendered fast to light and washing by coppering during or after dyeing. E.S.

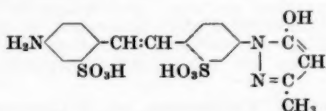
Metal(Copper and Nickel)-complex Disazo Stilbene Direct Dyes

Ciba BP 823,064

The Cu and Ni complexes of disazo compounds—



(X = CO-CH:CH-CO or preferably CO) are direct dyes, more stable in the dyebath than the similar dyes in BP 503,609 (J.S.D.C., 55, 464 (1939)) which have the Cl atoms in the terminal benzene nucleus in the *p*- instead of in the *m*-position relative to the azo link. Thus the stilbene pyrazolone compound—



n hue
E.S.

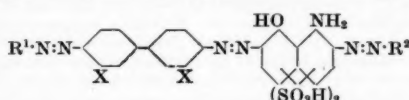
22,096
ng a
o the
xy-4-

is made into the urea derivative, by condensation of 2 mol. with 1 mol. of phosgene, which is coupled with 2 mol. of diazotised 4-chloroanthranilic acid. Heating at 70–80°C. with ammoniacal CuSO₄ gives the Cu-complex, which dyes cotton yellow. E.S.

Grey Metal(Copper)-complex Trisazo Dyes

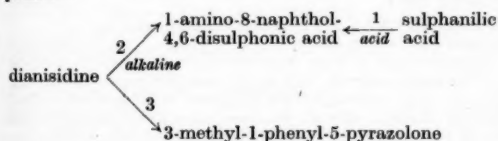
CFM BP 820,990

Copper complexes derived from trisazo compounds—



each
and
n the
ay be
noline
, etc.
d-2-
tised
xy-4-
acid

(X = COOH or OAlk; R¹ = phenolic or enolic coupling component other than salicylic acid and its derivatives; R² = aryl) are grey direct dyes of better solubility and wet fastness than the similar Cu-complexes of BP 771,330 (J.S.D.C., 73, 274 (1957)) in which R¹ = the residue of salicylic acid or its derivatives. Thus the trisazo compound—



ss to
E.S.

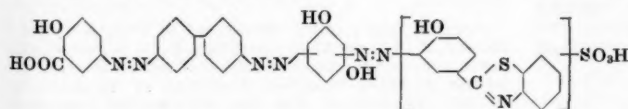
1,331

is heated in aq. ammoniacal CuSO₄ to give the Cu-complex which dyes cellulose reddish-grey, little altered in hue by application of a crease-resist finish. E.S.

Metallisable Trisazo Direct Dyes having a Thiazole Residue

Ciba BP 823,053

Trisazo compounds of the type—

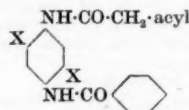


are direct dyes which may be metallised, particularly with Cu compounds, in substance in the dyebath or on the fibre. Thus (2(3'-amino-4'-hydroxyphenyl)benzthiazolesulphonic acid (prepared by sulphonation of the parent body made by the method of BP 359,063 (J.S.D.C., 48, 42 (1932)) is diazotised and coupled with 1 mol. of resorcinol, and the product is then coupled with the diazoazo compound made by coupling tetrazotised benzidine with 1 mol. of salicylic acid. The trisazo dye so formed gives browns on cotton by the single-bath or two-bath aftercoppering process. E.S.

Yellow and Orange Azoic Dyes from 3,3'-Dichlorobenzidine

Ciba BP 821,029

Tetrazotised 3,3'-dichloro(or 3,5,3',5'-tetrachloro)benzidine is coupled on the fibre with benzoyl(or aceto)acetylides—



(acyl = benzoyl or CH₃CO; one X = OCH₃ or OC₂H₅; the other X = Hal or preferably OCH₃ or OC₂H₅) to give yellows of high light fastness. Thus a thickened mixture of 4-benzamido-2,5-diethoxyacetanilide and the bis-triazene from tetrazotised 3,3'-dichlorobenzidine and methyltaurine, made alkaline with aq. NaOH, is printed on cotton, dried and steamed under acid conditions to give gold-orange. E.S.

Azo Dyes from Dextrans—Stains for Wood

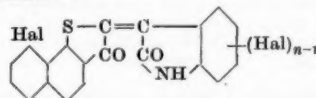
Commonwealth Engineering Co. of Ohio BP 823,221

Azo compounds made by coupling diazo compounds with dextrans, or by diazotising aminobenzoic esters of dextrans and coupling with e.g. β-naphthol, are soluble or dispersible in water to give stains for wood, and are compatible with fluorescent brightening agents, e.g. hydroxycoumarin, used in such stains. E.S.

Indigoid Dyes

Ciba BP 822,732

Brown vat dyes of good fastness to light and rubbing are of formula—



(n = 1 to 3). They are made by condensing an 8-halogeno-1,2-naphthoindoxyl with unsubst. or Hal-substituted isatin. Thus, 8-chloro-1-naphthylthioglycolic acid, chlorobenzene and PCl₅ are heated at 95°C.; AlCl₃ is added at 45°C. to give, by ring closure, 8-chloro-1,2-naphthoindoxyl and the vat dye is then formed by adding 5,7-dibromoindole in chlorobenzene to this reaction mixture and heating at 95°C. There are advantages in both preparation and properties over the similar dyes described in BP 233,031. E.T.

Azoic Dyes—Alkaline-earth Metal Salts of Triazenes from N-Alkyl-5-sulphoanthranilic Acids

FBY BP 821,926

N-Alkyl-5-sulphoanthranilic acids give triazenes with diazotised halogeno-anilines, -toluidines, or -anisidines which cannot be isolated by salting out, but can be readily separated and filtered off as their alkaline-earth metal salts; these salts regenerate the diazo compounds readily on neutral steaming and can thus be used for producing azoic dyeings and prints. Thus a diazo solution prepared from 2-amino-4-chlorotoluene is run into an alkaline solution of N-ethyl-5-sulphoanthranilic acid. Addition of CaCl₂ then gives the Ca salt of the triazene, precipitation of which is completed by adding NaCl. E.S.

Metal(Copper)-complex Azoic Dyeings and Prints

FBY BP 822,858

o-Aminomonoazo components, free of SO₃H and non-complex forming COOH groups, and having in the o'-position OH, COOH, or other groups capable of metal-

complex formation, are diazotised and coupled on the fibre with azoic coupling components. The resulting azoic dyeings or prints are treated with hot aq. CuSO₄, followed by soaping, to give greens, olives, browns, and greys. Or coupling may be effected in presence of a suitable copper compound, when a milder aftertreatment serves to develop the stable Cu-complex. Thus cotton yarn is impregnated at 25°C. with a soln. in aq. NaOH of the o-toluidide of 2-hydroxyanthracene-3-carboxylic acid containing the Cu salt of N-methyl-N-(2-hydroxyethyl)-glycine, and after squeezing, coupling is effected with a

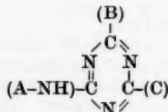
diazotization prepared from the aminomonoazo compound anthranilic acid—4-amino-2-methoxytoluene to give a blackish green. Boiling with aq. soap for 30 min. gives clear yellowish green. E.S.

Direct-dyeing Triazine Dyes

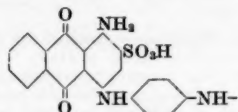
Ciba

BP 822,013

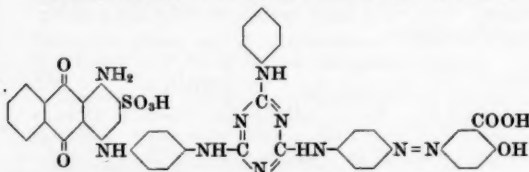
Dyes suitable for the direct colouring of animal or vegetable fibres and which, if they contain *o*-hydroxy-carboxy groups, may form metal complexes, are of formula—



(A-NH) = residue of a 1-aminoanthraquinone-2-sulphonic acid bound in the 4-position by a bridge member and an unsubst. benzene res.; e.g.—



(B) and/or (C) = -HN-R¹-N = N-R² in which R¹ is a benzene res. and R² is a benzene res. containing an OH group *para* to the azo link and a COOH group *ortho* to the OH. (B) or (C) = (A-NH) as above or a benzene residue attached through -NH- to the triazine ring. For example—



They are made reacting with the Hal atoms of cyanuric halide as follows—I. 1 mol. of H₂NR¹N = NR², 2 mol. of A-NH₂; II. 2 mol. of H₂NR¹N = NR², 1 mol. of A-NH₂; III. 1 mol. of H₂NR¹N = NR², 1 mol. of BH, 1 mol. of A-NH₂. E.T.

Reactive Dyes containing Pyrimidine Groups

ICI

BP 822,047

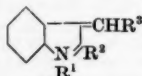
Azo, anthraquinone, phthalocyanine or nitro dyes which contain (a) < 1 amino group having at least 1 H atom attached to the N atom and (b) < 1 water-solubilising group, e.g., SO₃Cl, SO₃H or COOH, are reacted with 2,4,6-trihalogeno-pyrimidines. The products are 2,6-dihalogeno-4-pyrimidylamino- and 4,6-dihalogeno-2-pyrimidylamino derivatives of the water-soluble dyes. With azo dyes, the pyrimidylamino group may be present in one or both of the components before coupling. The dyes resulting from this process may be applied to silk, wool, regenerated protein or regenerated cellulosic fibres in presence of an acid-binding agent, e.g. NaOH, K phosphate, Na₂CO₃. Application to silk, wool, protein, polyamide, and polyacrylonitrile may be carried out in neutral or weakly acid dye baths. Dyeings on cellulosic fibres which have been treated with an acid-binding agent show good wet fastness. E.T.

Photographic Filter and Antihalation Dyes

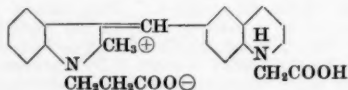
Agfa

BP 822,066

Dyes of formula—



(R¹ = H or Alk; R² = Alk, Ar, or subst. or unsubst. carboxyl; R³ = benzene having NH₂ in *p*-position or a heterocyclic ring containing at least one N atom), e.g. the violet—



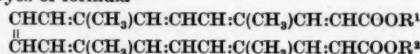
are used. Depending on the components used to form the dye it is possible to obtain dyes with most varied absorption ranges in the visible spectrum and in the adjoining infrared spectrum. When of suitable constitution they have a high grey content. C.O.C.

Bixin (C.I. 75120) and Norbixin Esters — Food Dyes

Chas. Pfizer & Co.

USP 2,891,087

Dyes of formula—



(R¹ = CH₃ or R²; R² = an etherified or esterified hydroxy-alkyl or polyhydroxyalkyl group) are obtained by treating a solution of trialkylamine salt of bixin or norbixin with an alkyl halogeno formate and then treating the resultant mixed anhydrides with a mono- or polyhydric alcohol in presence of a tertiary amine. Thus bixin dissolved in CHCl₃ was treated with triethylamine and the resulting salt treated with ethyl chloroformate. The bixin ethyl-carbonic mixed anhydride obtained was treated with a mixture of pyridine and ethyl alcohol and the resulting ethyl bixin purified by solution successively in chloroform and acetone, the solvent being removed in each case by evaporation, the dye being finally recrystallised from alcohol. C.O.C.

Microbiological Production of β-Carotene (C.I. 75130) and Related Carotenoids

U.S. Secretary of Agriculture

USP 2,890,989

A medium to be inoculated with a suitable organism and then fermented aerobically is made up of an assimilable C source, a source of assimilable N, a thiamin source and mineral nutrients. In addition a lipid material, a surface-active agent, and β-ionone are incorporated into the medium. Thus soybean oil meal (43 g./l.), acid-hydrolysed cornflour (23), KH₂PO₄ (0.5), and thiamin hydrochloride (1.0 mg./l.) were mixed together, sterilised and then 48-hr. old vegetative mycelium of *Blakeslea trispora* NRRL 2456(+) and NRRL 2457(-) (5 ml. each/100 ml.) were added. This was followed by addition of soybean oil and cottonseed oil (2 ml. each/100 ml.) and an alkyl aryl polyether alcohol (5 ml. of a 25% aq. soln. per 100 ml.), all these additions being sterile. The whole was incubated for 48 hr. at 28°C. and then 0–100,000 micrograms of β-ionone added per 100 ml. Incubation was then continued at 289°C. for a further 96 hr. The mycelium were then filtered off, dried, and the β-carotene extracted with petroleum ether. The yield of β-carotene varied from 2,800–34,000 micrograms per 100 ml. according to the amount of β-thionone used. C.O.C.

Carbon Black (C.I. Pigment Black 6 and 7)

Columbian Carbon Co.

USP 2,890,839

The structure of high structure Carbon Black is effected continuously, almost instantly and far more uniformly than by ball milling if the pigment is passed as a continuous uniform stream between two hard-surfaced rolls set to a clearance of > 0.030 in. and rotating at different speeds. This enables advantage to be taken of the high yields and production rates of the aromatic oils to obtain either high structure Carbon Blacks or normal "structure" Carbon Blacks similar to those obtained from natural gas or paraffinic oils. C.O.C.

Iron Urushiolate—Black Pigment for Lacquers, Moulded Plastics, Inks, etc.

K. Ohashi

BP 822,573

USP 2,891,978

Urushiol (the purified constituent of oriental lacquer, the sap of the tree *Rhus vernicifera*, D.C.) is heated with excess iron and the product extracted with a solvent, e.g. solvent naphtha, to obtain a solution of the colouring matter. Alternatively less than the chemical equivalent of iron is used and the product is mixed with a monohydric phenol and an addition product of hexamethylene tertamine and then heated to effect condensation after which the colorant is extracted by a solvent. The resulting pigment is deeply coloured and highly transparent. It has good miscibility with various types of synthetic resin. C.O.C.

Silicone-siliceous Pigment Dispersion

E. H. Phreaner and H. C. White

USP 2,891,875

Silica (C.I. Pigment White 27) when precipitated in presence of a liquid insoluble polysiloxane, preferably in oil, does not tend to agglomerate or polymerise. C.O.C.

Colour Characteristics of Copper Phthalocyanine (C.I. 74160) and its Chlorinated Derivatives (V below)
Solutions of Amylose and Fibres, Foils, etc. produced from them (VI p. 55)
Interaction between Dyes and Surfactants—II (VIII p. 56)
Direct Dyeing of Cellulose. VI—Aggregation of Direct Dyes (VIII p. 56)
Polarographic Examination of Vat Dyeing Solutions (XIV p. 63)

V—PAINTS; ENAMELS; INKS

Colour Characteristics of Copper Phthalocyanine (C.I. 74160) and its Chlorinated Derivatives
M. Shigemitsu

Bull. Chem. Soc., Japan, **32**, 693–695 (July 1959)

Colour variations with change of pigment concentration for copper phthalocyanine and some chlorinated derivatives in polymerised linseed oil are reported in C.I.E. notation. A.J.

Sorption to Paper of Cobalt Driers dissolved in Linseed Oil and the Significance of this for the Drying of Printing Ink
K. Cleerdin

J. Oil and Col. Chem. Assoc., **42**, 406–413 (June 1959)

The commonly experienced increase of drying time of printing ink on paper with increase in atmospheric R.H. is caused by increasing sorption of the Co and retardation by water of the linseed oil's autoxidation. The usual increase in drying time on lowering the paper's pH cannot be caused by increased sorption of the Co and seems to be caused by decrease in its catalytic activity. The mechanism of this decrease is discussed. C.O.C.

Enamel in 1958

H. J. van Buren *Chem. Weekblad.*, **55**, 276–283 (1959)
Chem. Abs., **53**, 17532 (25 Sept 1959)

Review, 105 references. C.O.C.

Properties and Application of Urethane Coatings

E. R. Wells, G. A. Hudson, J. H. Saunders, and E. E. Hardy
Off. Dig. Fed. Paint Yarn. Prod. Cl., **31**, 1181–1210 (Sept 1959)

PATENTS

Printing Inks of High Carbon Black Content

J. M. Huber Corp. *USP* 2,891,872

A printing ink suitable for high speed printing has a vehicle consisting of < 80% mineral oil hydrocarbon together with a dispersing agent and an antiflocculant. The ink contains at least 16% by weight of Carbon Black (C.I. Pigment Black 6 and 7). The ratio of yield value (dynes/sq.in.) to plastic viscosity (poises) is < 70 at 30°C. C.O.C.

Fluorescent Coating Compositions

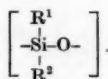
Industrial Colours *BP* 822,709

A vinyl chloride polymer or copolymer formed by emulsion or suspension polymerisation is, without intermediate drying, dyed with a fluorescent dye, e.g. C.I. Basic Yellow 3, and then dispersed in a liquid vehicle containing a film-forming material. C.O.C.

Black Coating of High Thermal Dissipation and Low Reflectivity

Westinghouse Electric Corp. *USP* 2,891,879

A mixture of finely powdered aluminium (1 part by wt.) and an organopolysiloxane resin (0.35–20.0) containing a recurring group—



(R¹ and R² = same or different, aliphatic, aromatic or hydrocarbonoxy), and, if desired, a solvent, is used. After it has been applied it is heated in a non-oxidising atmosphere at 660–1500°C. C.O.C.

Primers for Vinyl Chloride Resin Coatings (III p. 45)

Anomalous Spectrophotometric Behaviour of Copper Phthalocyanine—Benzidine Yellow (C.I. Pigment Blue 15—C.I. Pigment Yellow 12) Mixtures (IV p. 47)

Iron Urushiolate—Black Pigment for Lacquers, Moulded Plastics, Inks, etc. (IV p. 52)

VI—FIBRES; YARNS; FABRICS

Influence of Ginning Conditions and Subsequent Fibre Preparations on Certain Properties of Cotton Fabrics

AATCC Southeastern Section

Amer. Dyestuff Rep., **47**, 927–931 (29 Dec 1958)

Structure of Cellulose

A. I. Kitaigorodskii and D. Ya. Tavankin

High Molecular Weight Compounds, **1**, 269–292 (1959)

J. Polymer Sci., **38**, 563 (Aug 1959)

One-dimensional X-ray analysis appears to show that there are no crystalline and amorphous regions separated by definite boundaries, a typical structural element being a group of chains packed in poor three-dimensional order. P.T.S.

Infrared Spectra of Crystalline Polysaccharides. I—Hydrogen Bonds in Native Cellulose

C. Y. Liang and R. H. Marchessault

J. Polymer Sci., **37**, 385–395 (June 1959)

Two sets of intermolecular hydrogen bonds are proposed from the results of polarised infrared absorption measurements: in the 101 plane the C₆ hydroxyls of the antiparallel chains are joined to the bridge oxygens of the adjacent parallel chains; in the 101 plane the C₆ hydroxyls of the parallel chains are hydrogen bonded to the bridge oxygens of adjacent antiparallel chains. P.T.S.

X-Ray Study of Partially Benzoylated Cotton Cellulose

J. J. Creely, D. J. Stanonis, and E. Klein

J. Polymer Sci., **37**, 43–49 (May 1959)

Benzoylation causes mercerised cotton to assume a new, distended, crystal lattice even before the cellulose is fully benzoylated. Heat treatment improves the crystallinity. The (101) interference is the one affected by benzoylation, increasing from 7.35 Å. to 16.9 Å. P.T.S.

Chemical Modification of Flax Cellulose. I—Action of Acrylonitrile, Chloroacetic Acid, and β-Propiolactone

N. Gokal and J. K. Skelly

J.S.D.C., **75**, 486–493 (Oct 1959)

Sorption of Water Vapour by Cellulose and Polyvinyl Alcohol at High Humidities

T. Kawai

J. Polymer Sci., **37**, 181–198 (May 1959)

This treatment is an advance on previous work in that (i) a more accurate equation is used to determine the partial molar free energy change due to elastic deformation of the crosslinked polymer; (ii) the solution of water is considered to take place only in the amorphous region of the polymer and therefore the volume fraction of polymer in the amorphous region (not in the whole polymer) is used in the calculation; (iii) the possibility that the solvent-polymer interaction parameter may vary with the extent of the absorption is taken into account. The elastic contribution to the isotherm is quite considerable. The ratio of the molal volume of polymer between crosslinks to that of solvent is unexpectedly small, which would suggest that there are frequent junction points between polymer molecules in cellulose, and these restrict the swelling. P.T.S.

Changes in Fibre Structure of Viscose Rayon on Treatment with NaOH

A. Nakai

J. Soc. Textile Cellulose Ind. Japan, **15**, 85–89 (Feb 1959)

The effects of NaOH concentration, and of subsequent drying, are studied. The degree of crystallinity of the fibres is determined by the iodine adsorption method and the mean distance between the crystalline regions deduced from the equilibrium dye adsorption. A maximum increase in crystallinity occurs at NaOH concentrations of 4–6%; below 4% crystallisation alone occurs, but above 6% randomisation occurs; no further change takes place beyond 12%. After drying, no maximum is observed, the fibres showing a gradual increase in crystallinity with increasing NaOH concentration. The latter also causes increase in dye adsorption before drying, but after, a maximum occurs at about 6% NaOH beyond which dye adsorption decreases only slowly. L.P.

Effect of Coagulation on Structure of Regenerated Cellulose. I—Studies on Model Cellulose Gels Coagulated from Viscose by Two-bath Treatments

A. Nakai *J. Soc. Textile Cellulose Ind. Japan*, 15, 90–94 (Feb 1959)

Formation of gels is studied in (1) gelatinisation of viscose, and (2) regeneration of cellulose. By measurement of equilibrium dye adsorption, accessibility and lateral-order distribution, the effect upon fine structure of conditions in the Na_2SO_4 and H_2SO_4 baths is investigated. The degree of change in the gel structure during drying depends upon the amount of chain order in the less-ordered regions of the fresh gel, although the specific character of the fresh gel is retained. Lateral-order distribution curves of the various cellulose gels are given.

L.P.

Nature and Cause of "Canary" Coloration of Wool

J. A. Serra and R. M. Albuquerque

Publ. fac. cienc. univ. Lisboa, Sec. A.

Cient. invest. No. 5, 53 pp. (1956)

Vet. Bull., 27, Abstr. No. 1916 (1957)

Chem. Abs., 53, 17521 (25 Sept 1959)

Yellow discoloration of wool is caused by the action of the alkaline suint on keratin and depends on formation of β -thiobis-(α -aminoacrylic acid), having a >C:CHSCH:C< linkage; more intense coloration would result from formation of a >C:CHSSCH:C< linkage.

C.O.C.

Rabbit Fibres. XXVI—Comparison of the Stress-Strain Curves of Carroted Angora Rabbit Fibre and Various Modified Fibres

S. Okajima, S. Ikeda, and K. Mizukami

J. Soc. Textile Cellulose Ind. Japan, 15, 108–115 (Feb 1959)

Stress-strain curves of fibres carroted at 20°, 35°, and 50°C. show little difference. To determine the effect of the cystine link and hydrogen bond on the mechanical behaviour of the fibres, the stress-strain curve of an ammonium-thioglycollate treated fibre in buffer solution is compared with those of the untreated fibres in 50% urea and 50% LiBr (containing $>10^{-3}\text{M. Br}_2$). No essential difference can be detected between their 30% extension and recovery curves. It is therefore difficult to explain the relation between the shape of the stress-strain curves and the chemical modification involved during treatment.

L.P.

Wool Fibres in Deuterium Oxide

M. Feughelman, A. R. Harly, and T. W. Mitchell

Text. Research J., 29, 564–567 (July 1959)

Both the load-extension and stress-relaxation curves were compared in the yield region for single wool fibres in water and D_2O . A comparison was also made of the rate of penetration of the two liquid fronts into dry fibres. In all cases the D_2O acted in the wool fibre the same as water with the temperature of the fibre reduced by about 5°C.

S.B.D.

Mixture Regain of Speciality Hair and Fur Fibres

W. von Bergen

Text. Research J., 29, 586–588 (July 1959)

The moisture adsorptive and desorptive powers of mohair, alpaca, cashmere, vicuna, and camel hairs were similar to those of wool and exhibited the same hysteresis effect. The moisture regain of rabbit, beaver, and muskrat fur fibres was about 2% lower than the foregoing, being ~13% against ~15%.

S.B.D.

Action of Sulphuric Acid on Wool. III—Isolation and Analysis of Three Preparations from the Wool Fibre

R. L. Elliott, R. S. Asquith, and D. H. Rawson

J.S.D.C., 75, 455–460 (Sept 1959)

Effect of Alkali on Wool; Evidence Against Disulphide Exchange for the Reduction in Solubility

J. M. Swan

Text. Research J., 29, 665–667 (Aug 1959)

Effect of Temperature on the Felting and Dyeing Properties of Wool

D. R. Graham and K. W. Statham

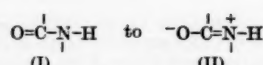
J.S.D.C., 75, 386–387 (July 1959)

Permanent Set, Supercontraction, Urea-bisulphite Solubility. The Proton Transfer Nature of Some Changes in Keratin and the Analogy with Muscle Contraction

P. T. Speakman

Nature, 184, 339–342 (1 Aug 1959)

In the reaction of cystine residues in keratin with OH^- ions, sodium bisulphite, etc., the proportion of



can alter. Increase in (II) will increase the strength of hydrogen bonds and this may account for the stability of permanently set keratin and keratin treated with alkali. It is an oversimplification to suggest that permanent set is entirely due to new covalent cross-links formed after reduction or hydrolysis of cystine residues. The first step in alkaline hydrolysis is probably ionisation of a proton from an α -carbon atom leading to a greater negative charge on the carbonyl oxygen which induces greater separation of charge on hydrogen bonding peptide groups. If proton transfer occurs between neighbouring peptide groups these will change from keto to enol forms. Hydrogen bonds involving enol forms will be stronger. Evidence for and against the view that in set β -keratin the main chain peptide links are in the enol form is reviewed and it is concluded that this is not the case. It is, however, suggested that cystine residues in equilibrium with alkaline solution spend some fraction of time in the ionised form causing increased negative charge on the carbonyl oxygen. This should induce greater separation of charges on a peptide group hydrogen bonded to it and on peptide groups hydrogen bonded to the first, leading to attraction of further peptide groups into the hydrogen bonded series of peptide groups and further groups being oriented into the α -helix of α -keratin of the parallel chains of β -keratin. X-Ray and infrared results agree with this view which is used to interpret steam setting. Similarity between contraction of muscle components containing sulphur and supercontraction of keratin is suggested.

W.R.M.

Kinetic Study of the Supercontraction of Wool Fibres in Aqueous Solutions of Acids, Alkalis or Salts

W. G. Crewther and L. M. Dowling

Text. Research J., 29, 541–549 (July 1959)

Wool fibres contracted in hot soln. of acids or alkalis, the rate of contraction increased with increasing concn. of the acid or alkali and the max. contraction obtained decreased. At the higher concn. contraction was followed by elongation. Comparison of the rates of contraction of wool fibres in soln. of different salts in N- and 4N-HCl showed that cations and anions fell into the following order of decreasing contraction rate $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ and $\text{I}^- > \text{Br}^- > \text{Cl}^-$ kinetic curves for contraction of fibres in N-HCl containing 4–6 M. salts showed well defined two-stage contraction. This was interpreted in terms of contraction at different rates of two structures in the wool fibre. S.B.D.

Action of Mixed Solvents on Wool

J. C. Atkinson, A. Filson, and J. B. Speakman

Nature, 184, 444 (8 Aug 1959 Suppl)

The behaviour of wool fibres in mixtures of primary alcohols and water and other mixed solvents has been studied. Interesting results are obtained with mixtures of n-propanol and water. The percentage change in resistance to 30% extension was determined. Maximum weakening is obtained with a mixture containing 45% (w/w) propanol. Weakening is accompanied by swelling. There are similarities between the action of aqueous solutions of different primary alcohols in modifying the elastic properties of wool and in dissolving zein. It seems likely that amide and inert side chains of keratin are grouped in such a way that some sections of the chains resemble those of zein and that cohesion between such sections is weakened by the same solvent action which causes solution of zein in aqueous propanol.

W.R.M.

The Relation between Configuration of Fibrous Proteins and their Chemical Structure

N. S. Andreeva

High Molecular Weight Compounds, 1, 315–323 (1959)

J. Polymer Sci., 38, 565–566 (Aug 1959)

Departure from a completely random arrangement of amino acid residues in the protein chain gives rise to specific configuration in individual chain fragments.

P.T.S.

Ultracentrifuge and Related Studies on Oxidised Wool Keratin

N. Peacock and F. O'Callaghan

J. Polymer Sci., 36, 485–498 (April 1958)

An investigation into the sedimentation behaviour of solutions prepared by oxidising Lincoln and Merino wools

by peracetic acid and extracting with 0.15 N ammonia. The sedimentation pattern shows two peaks. The effects of heat, fractionation, and precipitation on the proportion of the components was examined. P.T.S.

Glucosides of Jute. II—Structure of Olitoriside

N. K. Abubakirov, V. A. Maslennikova, and M. B. Gorovits
Zhur. obshch. khim., **29**, 1235–1240 (April 1959)

The fermentative hydrolysis of olitoriside $C_{32}H_{52}O_{14}$, a diglucoside from the seeds of *Corchorus olitorius* L., yields d-glucose and the $C_{28}H_{44}O_{12}$ residue, the latter giving on mild acid hydrolysis d-boivinose and strofantidin. A comparison of the mol. rotations shows the sugars in both cases to be linked with β -glucosidic bonds. The structure of olitoriside is given as strofantidin-(3)- β -d-boivinoside- β -D-glucoside. G.J.K.

The Photochemistry of Cellulose Acetate

J. Jortner *J. Polymer Sci.*, **37**, 199–214 (May 1959)

A study of the photodegradation of cellulose acetate by near ultraviolet light in air. P.T.S.

6,6-Nylon Molecular Weight Distribution

G. J. Howard *J. Polymer Sci.*, **37**, 310–313 (May 1959)

A very careful fractional precipitation of 6,6-nylon as a liquid precipitate was carried out using a *m*-cresol/cyclohexane system. The results, unlike those from some other workers, agree, within the limits of experimental error, with the molecular weight distribution predicted by Flory. P.T.S.

Temperature Dependence of the Deformation of 6,6-Nylon

G. L. Slonimskii and V. A. Ershova

High Molecular Weight Compounds, **1**, 240–243 (1959)

J. Polymer Sci., **38**, 562 (Aug 1959)

Crystal Structure in Polyamides made from ω -Amino Acids

W. P. Slichter *J. Polymer Sci.*, **36**, 259–266 (April 1959)

6-, 7-, 8-, 10-, and 11-Nylon were studied; those with an even number of carbon atoms have a hexagonal-like structure, those with an odd number of carbon atoms have a triclinic-like structure. P.T.S.

Re-equilibration of Poly- ω -aminocaproic Acid. Masking of Amino and Carboxyl Endgroups Due to a Reaction with an Isocyanic Acid Ester

G. M. van der Want *J. Polymer Sci.*, **37**, 547–549 (June 1959)

Rate of Formation of ϵ -Caprolactam upon Equilibration of Extracted Poly- ϵ -aminocaproic Acid Polymers

D. Heikens, P. H. Hermans, and S. Smith

J. Polymer Sci., **38**, 265–268 (July 1959)

Molecular Structure of Synthetic Fibres. XIV—Physico-Chemical and Mechanical Properties of Polycapramide and Polyundecanamide Polyamides

N. V. Mikhailov, T. I. Shein, V. O. Gorbacheva, and V. N. Topchibasheva

High Molecular Weight Compounds, **1**, 185–190 (1959)

J. Polymer Sci., **38**, 559–560 (Aug 1959)

Molecular Structure of Synthetic Fibres. XV—Thermochemical Properties of Polycapramide and Polyundecanamide Polymers

N. V. Mikhailov and E. Z. Fainberg

High Molecular Weight Compounds, **1**, 201–207 (1959)

J. Polymer Sci., **38**, 560 (Aug 1959)

Molecular Structure of Polyamide Fibres. XVII—Sorption Properties of Polyamide Fibres as a function of their Structure

Z. G. Serebryakova and N. V. Mikhailov

High Molecular Weight Compounds, **1**, 222–229 (1959)

J. Polymer Sci., **38**, 561 (Aug 1959)

By changes in the process of drawing fibres from the melt, amorphous and crystalline fibres can be produced with the same sorption characteristics—these are not merely functions of the crystalline-amorphous ratio, but also of the "packing density". P.T.S.

Electron Microscope and Electron Diffraction Investigations of the Crystalline Texture of Polyamides

A. Keller (appendix by A. Keller and R. Engleman)

J. Polymer Sci., **36**, 361–387 (April 1959)

6,6- and 6,10-Nylon were used. Spherulites appear to arise from the curling of flat sheets. Electrons destroy the

diffracting ability of crystals without affecting their shape. Polymer molecules lie at large angles to the length of even the smallest fibrils. This requires a regular, sharply-folded molecular configuration, which would also account for the uniform width of the microfibrils. P.T.S.

Natural and Artificial Ageing of High Polymer Fibres

A. Sippel *Kunststoffe*, **49**, 626–631 (Nov 1959),

German Plastics Digest (condensed English translation)

49, (II), 35–39 (Nov 1959)

The ageing of high polymer fibres can be studied by determining changes in mechanical strength and degree of polymerisation. The relationship between these two variables is the same for degradation by photolysis and by heat. Under the influence of catalysts, ageing, i.e. degradation rates, may increase without actual change of the constants of the equation that describes the relationship between changes in mechanical strength and degree of polymerisation. One of the constants of the equation is a sort of material constant and determines simultaneously stability to light and the electrostatic behaviour of the pure fibre substance. C.O.C.

Moisture Permeability of Polymers. I—Role of Crystallinity and Orientation

S. W. Lasoski and W. H. Cobbs

J. Polymer Sci., **36**, 21–33 (April 1959)

The water vapour permeability of polyethylene terephthalate, 6,10-nylon, and polyethylene films is equal to the water vapour permeability of the amorphous region multiplied by the square of the amorphous fraction. P.T.S.

Strain-induced Crystallisation in Polyethylene Terephthalate

A. B. Thompson

J. Polymer Sci., **37**, 313–315 (May 1959)

A theoretical note on viscoelastic extension during drawing. P.T.S.

Acrylonitrile Polymerisation Kinetics

A. G. Parts *J. Polymer Sci.*, **37**, 131–145 (May 1959)

A kinetic study of the polymerisation of acrylonitrile in aqueous solution by a ferric-hydrogen peroxide initiator. The inhibition by dissolved oxygen and the rate of decomposition of hydrogen peroxide are examined. P.T.S.

Dimensional Changes of Textile Fibres on Calendering

W. Bobeth *Melliand Textilber.*, **40**, 913–918 (Aug 1959)

Length changes on calendering a wide range of textile fibres under different pressures in a laboratory machine are reported in detail. They can be used for estimating the degree of fixation of Perlon. Whereas natural and regenerated protein fibres are most resistant to deformation under high pressures, polyester fibres are outstanding with low pressures, but become inferior to polyamides at intermediate pressures. S.M.J.

PATENTS

Softening Hard Vegetable Fibres

R. H. Turnbull

BP 822,323

Sisal fibres, etc. are treated with a liquor containing a cytase to soften them and are then repeatedly rolled to further soften them. C.O.C.

Solutions of Amylose and Fibres, Foils, etc. produced from them

Coöperatieve Verkoop en Productievereniging van Aardappelmeel en Derivaten, "Avebe" GA

BP 822,587

Addition of an aldehyde, e.g. formaldehyde, to an aqueous amylose system before, during or after its preparation, enables stable strong solutions of amylose to be obtained, e.g. a solution stable for at least 6 weeks containing 20–40% by wt. of amylose and 7% of formaldehyde. These solutions are highly viscous and so can be extruded to form fibres. C.O.C.

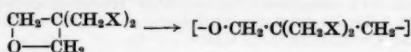
Fibres, Films, etc. from 3,3-bis(Substituted Methyl)oxetane

DuP

USP 2,891,837

A 3,3-bis(substituted methyl)oxetane is extruded into an inert fluid containing phosphorus pentafluoride. The oxetane polymerises immediately it contacts the phosphorus pentafluoride and can be drawn off as a filament,

film or other extruded shape. The polymerisation proceeds according to the equation—



C.O.C.

Investigations on Dissolving Pulp. XVIII—Microscopic Studies on Swelling and Dissolution of Cellulose (XI p. 60)

Action of Soda Solutions on Native Cellulose. Formation of Hydrated Sodium Cellulosate (XI p. 60)

Effect of Calcium Thiocyanate Solutions on Cellulose (XI p. 61)

Oxidative Degradation of Alkali Cellulose through Oxygen and Air (XI p. 61)

VII—DESIZING; SCOURING; CARBONISING; BLEACHING

Non-ionic Detergents in Raw Wool Scouring including Studies of Waste Clarification

W. Fong *Amer. Dyestuff Rep.*, 48, 45–50 (12 Jan 1959)

Effect of Phosphates and Silicates on Raw Silk. V—Effect of Condensed Phosphate in the Fermentative Degumming of Raw Silk

E. Ohmura and A. Hirata

J. Soc. Textile Cellulose Ind. Japan, 15, 129–131 (Feb 1959)

Pyrophosphates are effective agents for eliminating oily substances and in large amounts give the finished article a white appearance. Sodium metasilicate has the greatest effect on degumming whereas pyrophosphate and hexametaphosphate show the least. The finished cloth has the best handle when soap-degummed, sodium metasilicate or hexametaphosphate giving a very harsh handle. L.P.

Thermal Decomposition of Sodium Chlorite Solutions during Impregnation Bleaching of Cotton

F. Kassack and G. Berndt

Melliand Textilber., 40, 1031–1035 (Sept 1959)

Extensive investigations support the equations for decomposition of chlorite proposed by Hefti (*Ph.D. Dissertation, E.T.H., Zürich*, 1955) for long liquors, but their relative importance is very different in the short liquors used in impregnation bleaching. Thus ClO_2 evolution according to $5\text{ClO}_2^- + 2\text{H}^+ \rightarrow 4\text{ClO}_2 + \text{Cl}^- + 2\text{OH}^-$ is greatly reduced, and decomposition takes place overwhelmingly according to $\text{ClO}_2^- \rightarrow \text{Cl}^- + 2\text{O}$, the actual bleaching reaction. The changed emphasis is brought about by the fabric, not by the higher concn. of NaClO_2 . Natural impurities catalyse the bleaching action, greatest with the least pure cotton. The authors postulate hydrolysis of transiently formed ClO_2 according to $2\text{ClO}_2 + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{O} + \text{Cl}^- + \text{ClO}_2^-$, generating acidity during bleaching. Acid-producing activators like RCONH_2 depress evolution of free chlorine dioxide at all temperatures, and increase effectiveness of the bleach above 75°C. S.M.J.

Hydrogen Peroxide Bleaching

W. L. Lead and A. S. Ramadan

J.S.D.C., 75, 384–386 (July 1959)

Does Drycleaning Wear Out Clothes?

D. S. Lyle

Amer. Dyestuff Rep., 47, 917–924, 949 (29 Dec 1958)

A two-year wear study carried out in the U.S. National Institute of Drycleaning has shown that drycleaning alone does not wear out clothes. C.O.C.

PATENT

Chlorite Bleaching

FH

BP 822,603

The goods are impregnated with chlorite solution at pH 3.5–5.0 and then kept in air at 40–73°C. until the desired bleach is obtained. Thus Egyptian cotton poplin is impregnated at 60°C. with its own weight of a solution containing 80% aqueous sodium chlorite solution (19 g./l.), alkylaryl sulphonate (3) and methyl taurine (1.5) at pH 4.8 and then kept for 5 hr. at the impregnation temperature before being rinsed with hot and cold water and dried. This yields a full white. C.O.C.

Influence of Various Additives on Soiling and Soil Removal Characteristics of Knitted Fabrics (X p. 59)

Modifying the Properties of Polyester Fibres and Foils (X p. 60)

VIII—DYEING

Interaction between Dyes and Surfactants—II

T. Kondo, K. Meguro, and H. Nito

Bull. Chem. Soc. Japan, 32, 857–861 (Aug 1959)

A study of the interaction between a number of acid and direct dyes and dodecyl pyridinium bromide and between basic dyes and sodium dodecyl-sulphate. The acid dyes are flocculated on first addition of the surfactant and deflocculate at higher concentration. Values of deflocculation No. (see *J.S.D.C.*, 75, 505 (Oct 1959)) fall with increasing solubility of the dye, i.e. increasing affinity for water. Acridine Yellow (C.I. 46025) and Methylene Blue (C.I. Basic Blue 9) behave likewise, but Methyl Violet (C.I. Basic Violet 1) and Methyl Green (C.I. 42590) are unaffected. This is ascribed to greater resonance, resulting in smaller localisation of the positive charge and hence less interaction with the surfactant anion. With direct dyes the behaviour is more complex and is related to the aggregating properties of the dyes. A.J.

van der Waals and Dispersion Forces

W. L. Lead

J.S.D.C., 75, 460–461 (Sept 1959)

Direct Dyeing of Cellulose. VI—Aggregation of Direct Dyes

K. Nishida

J. Soc. Textile Cellulose Ind. Japan, 15, 52–55 (Jan 1959)

The aggregation number is found to decrease in the following order—Nippon Sky Blue (C.I. Direct Blue 15) > Aizen Direct Blue BBH (C.I. Direct Blue 6) > Diamine Blue 3B (C.I. 23350) > Dianil Azurine G (C.I. Direct Blue 8) > Congo Red (C.I. Direct Red 28) > Benzopurpurine 4BKX (C.I. Direct Red 2) > Azo Blue (C.I. Direct Violet 39) > Azoroseillin [sic]. The affinity of these dyes for cotton first increases with decreasing aggregation number and then decreases. The abnormally low values of Azoroseillin and Azo Blue are attributed to chelation within the molecule. L.P.

Dyeing of Dead Cotton Fibres

N. P. Solov'ev, N. G. Lysova, and M. N. Nikulova

Tekstil. prom., 19, 43–46 (June 1959)

Cotton sliver containing appreciable amount of dead fibres can be successfully dyed at temp. up to 133°C. without further loss in strength compared with identical dyeing below 100°C. No wetting agents are required, thus retaining the wax content necessary for spinning. Sulphur, vat, and direct dyes are used. G.J.K.

Adsorption of Arylamides of 2-Hydroxy-3-naphthoic Acid and Related Compounds by Cellulosic Fibres

E. H. Daruwalla and R. H. Mehra

Text. Research J., 29, 595–610 (Aug 1959)

The adsorption of these azoic coupling components under different conditions was studied by varying the alkali concn., salt concn., and temperature amongst others. Limitations of Marshall and Peters thermodynamic treatment for calculation of affinity values were indicated and a modified treatment was developed in which consideration was given to the simultaneous adsorption of hydroxyl ions on the accessible hydroxyl groups in the fibre. Heats of adsorption and entropy changes during application were calculated for three arylamides. Correlation between affinity values of arylamides and their chemical constitutions was also established. S.B.D.

Fast Dyeings on Wool—Cellulosic Unions

D. R. Lemm and J. K. Collins

J.S.D.C., 75, 421–429 (Aug 1959)

Effect of Mordant Dyes on the Tensile Strength of Wool

J. Hornung and K. Székér

Magyar Textiltechnika, 10, (3), 101–102 (1958)

Hungarian Tech. Abs., 11, (1), 18 (1959)

The action of individual factors on the tensile strength of wool in the course of dyeing was determined in laboratory and works tests. Even distilled water causes a 5–10% reduction of strength during a 4 hr. boil. Of formic, sulphuric, and acetic acids, formic acid proved to be the least deleterious at identical concentrations. This was

also true when potassium bichromate or dyes were present. Dyeing with formic acid resulted in 13–14% loss of strength whereas with sulphuric or acetic acid there was 17–19% loss. The harmful effect of potassium bichromate is lessened by acids. Of the salt additives Na_2SO_4 caused less reduction in strength than NaCl. C.O.C.

Oxidative Dyeing of Wool

A. I. Levenchenko *Tekstil. prom.*, 19, 48–52 (June 1959)
Wool, unions, and furs can be dyed with amino derivatives of carbazole, dihydroxynaphthalenes, aminocarboxylic-, hydroxycarboxylic-, and aminohydroxy sulphonic acids by oxidative processes, using $\text{K}_2\text{Cr}_2\text{O}_7$, CuCl_2 , NaClO_3 , H_2O_2 , leading to the formation of quinone dyes on the fibre. Dyeing conditions, shades, and fastness properties are tabulated. G.J.K.

Copper Aftertreatment of Dyed Union Fabrics

F. Péter and B. Mihálik
Magyar Textiltechnika, 10, (3), 120–122 (1958)
Hungarian Tech. Abs., 11, (1), 18 (1959)

The fastness of copper-aftertreated union fabric colourings, the rate of copper pick-up and the amount of copper bound in the equilibrium state are strongly influenced by the temperature of treatment. Copper absorption and fastness to washing, water, light and rubbing of white wool and of fabrics dyed with "Halbwollkuprophénolmarineblau 2RL" were examined as a function of time subsequent to aftertreatment at 30, 60, and 100°C. Copper absorption of the undyed fabric approaches that of the dyed cloth at higher temperatures, the state of equilibrium is reached at all three temperatures within a comparatively short time (20 min.). Rate of absorption increases at higher temperatures. The amount of copper absorbed at equilibrium also increases with increase in temperature and light fastness as well as fastness to washing are improved without lessening fastness to rubbing. The copper content of the bath was determined by polarography which gives quick and accurate determination of small concentrations of copper. Measurements were carried out in ammonia-ammonium chloride medium because it gave the best conditions for the accurate evaluation of the polarogram. C.O.C.

Jigger Studies. I—The Watering of Acetate Poults

E. France *J.S.D.C.*, 75, 477–483 (Oct 1959)

Physical State of Direct Dyes in Viscose Rayon and its Influence on Light Fastness

L. Weissbein *J.S.D.C.*, 75, 537 (Nov 1959)

Sorption of Congo Red by Poly(vinylalcohol) Film

K. Fujino and F. Fujimoto
J. Soc. Textile Cellulose Ind. Japan, 15, 138–141 (Feb 1959)

Adsorption isotherms on heat-treated PVA films are given at 45, 60, and 70°C. The initial part of the isotherm is of a Langmuir type which at higher concentrations becomes simple partition. The amount of adsorbed water in the film affects the amount of dye adsorbed. L.P.

Some Observations on Dyeing by the Cuprous-ion Method

D. R. Graham and K. W. Statham
J.S.D.C., 75, 452–455 (Sept 1959)

Dyeing Unions containing Acrylic Fibres

B. Kramrisch *J.S.D.C.*, 75, 364–373 (July 1959)

Uses of Acrylic Fibre Blends with reference to Colour Fastness

H. D. Edwards and N. Jackson
J.S.D.C., 75, 383–384 (July 1959)

Dyeing of Polyester Fibres and Blends

H. W. Partridge *J.S.D.C.*, 75, 373–378 (July 1959)

Carrier-assisted Dyeing of Hydrophilic Fibres

AATCC Delaware Valley Section
Amer. Dyestuff Rep., 47, 789–795 (17 Nov 1958)

Use of carriers as dyeing assistants, generally thought to be limited to the dyeing of hydrophobic fibres, is in fact generally applicable with all fibres. The mechanism of the action of carriers in wool dyeing (and of other fibres generally) is that the carrier is absorbed by the fibre. This makes the fibre more permeable to dyes and so increases the dyeing rate. The solvent layer theory is untenable both on theoretical and experimental grounds. C.O.C.

Dyeing Orlon

L. Bidgood and W. Bell

Amer. Dyestuff Rep., 48, 51–54 (12 Jan 1959)

An account of improved methods for dyeing Orlon/Dacron blends. A one-bath method is described which enables better and quicker matching than is possible by the two-bath process. Cationic dyes are now available which enable Orlon to be dyed to withstand 500 hr. in the Weather-Ometer. C.O.C.

Absorption Spectra of Dyes. VII—Deformation of the Absorption Spectra of Some Dyes in PVA Films when subjected to Dry Heat

Y. Ishii
J. Soc. Textile Cellulose Ind. Japan, 15, 582–588 (1959)

Poly(vinylalcohol) films were heated in paraffin at 125, 150, 180, and 200°C. They were then dyed with Benzo Azurine G (C.I. Direct Blue 8) (A), Enianil Azurine J (C.I. Direct Blue 152) (B), Benzo Purpurine 10B (C.I. Direct Red 7) (C), Congo Red (C.I. Direct Red 28) (D), and γ -acid-tetrazotised dianisidine (E). The spectra of films dyed with A or E are affected by the temperature of the paraffin bath. Deformation of the absorption curves of the dyed films caused by dry heat can be divided into 3 classes: (1) the peak and shoulder on the longer wavelength side of the curve shift toward the shorter wavelength and both extinction coefficients are reduced (for dyes A and E); (2) the curves do not shift but are reduced without any deformation (for dyes C and D); (3) the complex deformation of these curves is measured (for dye B). The colour change caused by dry heat is irreversible but the original colour is restored by wetting and drying the film. C.O.C.

PATENT

Dyeing or Printing Polyamides, Polyurethanes, Poly(vinyl Alcohols) or Modified Polyacrylonitriles with Disperse Dyes containing a Monohalogeno-1,3,5-triazin-2-ylamino Group

ICI BP 822,500

Water-insoluble dyes free from ionogenic solubilising groups or intermediates which can be converted on the fibre into such dyes give dyeings or prints which are faster to washing than those hitherto obtainable with disperse dyes. Thus the dye (1 part) obtained by reacting 4-amino-2'-hydroxy-5'-methylazobenzene with 1 mol. of 2-methoxy-4,6-dichloro-1,3,5-triazine is dispersed in water (20) and the dispersion added to water (4000) containing a fatty alcohol-ethylene oxide condensate (4). Nylon cloth (100) is then placed in the liquor which is then brought to 95°C. and kept at that temperature for 60 min. The cloth is then treated with a hot aqueous solution containing 0.1% of soap and 0.1% of Na_2CO_3 , rinsed and dried. It is dyed yellow of very good fastness to washing. C.O.C.

Ageing of Sulphur Dyes (IV p. 48)

Remazol (FH) Colours: a Chemically new System of Reactive Dyes (IV p. 48)

Effect of Temperature on the Felting and Dyeing Properties of Wool (VI p. 54)

Polarographic Examination of Vat Dyeing Solutions (XIV p. 63)

IX—PRINTING

Manufacture of Printed Cloths in India in the 18th Century

P. R. Schwartz

J. Indian Textile History, (2), (156); (3), (1957)
Bull. Soc. Ind. Mulhouse, (689), 137–152 (1957); (693), 22–31 (1958)

A discussion and commentary, illustrated with colour plates, of a manuscript in the central library of the Muséum national d'histoire naturelle, Paris. In it are described the methods used in Pondicherry in 1736. C.O.C.

Emulsion Thickenings—Possibilities in Textile Printing

T. L. Dawson

J.S.D.C., 75, 413–421 (Aug 1959)

Colloidal Factors in Textile Pigment Printing Emulsions

E. Nelson *Amer. Dyestuff Rep.*, **48**, 1-4, 36 (12 Jan 1959)

A survey of the most important formulation factors common to these emulsions. The fundamental components of these emulsions—(a) pigment, (b) emulsifying or dispersing agent, (c) vehicles or binders, and (d) thinners or solvents, are each discussed as are the colloidal theories of emulsions. C.O.C.

Coloured Discharges on Polyamides with Anthrasol Dyes

E. Feess *Melliand Textilber.*, **40**, 1042-1045 (Sept 1959)

Anthrasol dyes are advocated for coloured discharge printing of nylon. Steaming is followed by development with nitrite in sulphuric acid. 1:2-Metal complex dyes are preferred for the grounds, and recommended examples from the Remalan, Isolan, and Vialon ranges are listed. S.M.J.

Printing with Metallic Powders

M. Mackay

Text. Manuf., **84**, 405 (Sept 1959)

Bright sharp patterns can be obtained if printing procedure is modified to suit the peculiarities of metal pigments. Preparing is usually the same but it is advantageous to calender before printing to form a flatter surface that retards penetration of the printing paste. With flannels it has been found beneficial to use a Schreiner calender to flatten the nap. The metal pigment should pass through screens of 285-325 meshes/in. Smaller particles do not bind well and larger ones have poor light reflection. It is usually best to mix only enough paste for 2-3 hr. working. Any left overnight should be mixed with 10 times as much fresh paste. The printing rollers should have coarse grounds etched so that they resemble the teeth of a file in the bottom of the engraving. Too-fine grounds tend to become clogged with metal particles. Unbroken lines around the roller that are too fine to be ground should be avoided because any foreign matter trapped under the doctor blade will strip the paste out of the engraving and the line will not print. Straight copper rollers give better coverage than chromium-plated rollers; metal powders do not scratch the copper which seems to give better adhesion of the paste. Because of the deep engraving and shallow grounds, rollers for metal printing are seldom suitable for use for other purposes. The roller should be set lightly against the fabric as heavy pressure drives the binder into the fabric and leaves the pigment metal on the surface with not enough binder to hold it. To stop other pastes in the pattern contaminating the metal print, a gum roller is often used ahead of the metal print roller and the latter has a lint doctor on it. A better reflective surface is obtained by calendering the prints before they are soaped. C.O.C.

PATENTS

Developer for Electrostatic Printing

General Dynamics Corpn.

USP 2,891,911

A mixture of an opaque powder, a high resistance liquid and an ingredient to fix the opaque powder when the temporary image is contacted with a permanent record medium, is used. Thus a mixture of Carbon Black (C.I. Pigment Black 6 and 7), kerosene and polyethylene of mol.wt. 2000 produces a good temporary image. When transferred to a permanent record medium and heated to slightly above the m.p. of the polyethylene it yields a good permanent image of good fastness to rubbing. C.O.C.

Colour-corrected Colour Photographs

Agfa

BP 822,125

Colour correction is obtained by heating the colour images with a solution, preferably an aqueous solution, of an azide. The azide forms a masking dye image from the residual colour coupler. C.O.C.

Colour Photography

Agfa

BP 822,616

Substantial improvement in colour reproduction is produced with multi-layer materials by using filter layers containing one or more dyes which are present in a diffusion-resisting and highly associated form and produce absorption bands which are so positioned that undesirable green sensitivity in the sublayer sensitised for red is much reduced. C.O.C.

Remazol (FH) Colours: a Chemically new System of Reactive Dyes (IV p. 48)

Dyeing or Printing Polyamides, Polyurethanes, Poly-(vinyl Alcohols) or Modified Polyacrylonitriles with Disperse Dyes containing a Monohalogeno-1,3,5-triazin-2-ylamino Group (VIII p. 57)

Polarographic Examination of Vat Dyeing Solutions (XIV p. 63)

X—SIZING AND FINISHING

Investigation of Inorganic Salts and Oxides as Finishes for Cotton

R. M. Esteve, G. E. Wright, and P. B. Mack

Amer. Dyestuff Rep., **48**, 139-142 (21 Sept 1959)

Of 74 compounds studied the following gave promise of being of use as finishes for cotton cloth, aluminium hydroxide, beryllium oxide, cobaltous hydroxide, cobaltous metaborate, lead hydroxide, manganous oxide, manganous phosphate, manganous silicate, and nickelous phosphate. Of those yielding white or cream cloths some gave improved resistance to weathering while others gave some resistance to atmospheric contamination, some degree of flame resistance, and some water repellency. Lead hydroxide-finished cotton was a white cloth which differed from the other white fabrics in having no resistance to weathering although it had very good resistance to atmospheric contamination. In addition it had the best resistance to burning and very good water-repellency. The compounds yielding coloured finishes had improved resistance to water. Cobalt metaborate-treated fabric had excellent resistance to mildew and rotting, weather, actinic degradation and atmospheric contamination and had excellent water repellency. Cobaltous hydroxide-treated fabric had the same excellent properties except for water repellency. The manganese and nickel compounds were much inferior to the cobaltous compounds in these respects. C.O.C.

Phenolic-formaldehyde Resins as Finishing Agents for Cotton Fabrics

L. H. Chance, F. S. Perkerson, and O. J. McMillan

Text. Research J., **29**, 558-564 (July 1959)

Cotton fabric was treated with halogenated and unhalogenated phenolic-formaldehyde resins and the properties of the fabric evaluated. The resins were applied by padding the fabric through a soln. of the phenol in alkaline formalin, drying, and curing in an oven. All the fabrics had improved rot resistance and crease recovery, the halogenated phenols having no significant advantage in imparting rot resistance. Fabrics treated with *m*-chloro- and *m*-bromophenol had the best crease recovery. S.B.D.

Crease Recovery by Urea-Formaldehyde Resin. II—The Mechanism of the Crease Recovery Finish

M. Hida

J. Soc. Textile Cellulose Ind. Japan, **15**, 46-51 (Jan 1959)

The relation between the amount of bound formaldehyde and crease recovery imbibition value and elasticity of viscose rayon fabrics is measured, together with the effect of repeated soaping. A concentration of up to 4% bound formaldehyde causes a considerable change in these properties, but further increase has little effect. Improvement in crease recovery and decrease in imbibition value are proportional to increase in elastic recovery; repeated soaping causes little change in these results. Apparently formaldehyde forms a cross-linkage between two hydroxyl groups of adjacent cellulose chains. L.P.

Chelating Agents in Resin Finishing

AATCC Rhode Island Section

Amer. Dyestuff Rep., **47**, 797-801 (17 Nov 1958)

Addition of organic chelating agents to the resin liquor has a beneficial effect upon some physical properties of the finished fabric. The effects produced vary with the chelating agent and the type of resin used. In many cases increases in tensile strength and tear strength and reduction in damage caused by chlorine retention after several washings were obtained. C.O.C.

A Brief Look at Wash-Wear Finishing

A. C. Nuessle

Amer. Dyestuff Rep., **47**, 885-7 (15 Dec 1958)

Brief survey of the status of wash-wear finishing in the U.S.A. C.O.C.

Rotproofing Cellulosic Textiles

M. Gopal, R. M. Desai, and V. B. Chipalkatti
16th All India Textile Conference and Industrial Exhibition
 Souvenir, 17-25 (May 1959)

A review of the literature, 84 references. C.O.C.

Some Properties of Flameproof Fabrics

M. W. Sandholzer

Amer. Dyestuff Rep., **48**, 37-41 (26 Jan 1959)

A series of tests carried out on five different cotton and rayon cloths with 7 different flame-retardant finishes, using samples before and after laundering up to 14 times, showed that several of the finishes had good durability to washing. Commercial finishes were most successful on closely woven fabrics of medium or heavy weight. Generally the finishes caused reduction in tearing strength but did not significantly affect breaking strength.

C.O.C.

Increased Wear Resistance of Mercerised Cotton Hosiery

E. T. Ustinova and L. I. Zvereva

Tekstil. prom., **19**, 42-43 (June 1959)

Mercerised hosiery treated with an aq. emulsion of polymethacrylate and chitosan preparation shows increased wear resistance of 50-80% combined with a soft handle and elasticity.

G.J.K.

The Setting of Wool Fabrics

F. Bekku

J. Soc. Textile Cellulose Ind. Japan., **15**, 35-45 (Jan 1959)

III—Effect of pH

The effect of pH on the setting of fibres and fabrics is determined by measuring the shrinkage produced on soaking. The rate of setting, and its relation to pH, is also studied and comparison made between fibres and fabrics. The more alkaline the setting bath the greater the shrinkage; this effect applies to fabrics only. The magnitude of the pH effect depends also on the temperature of the setting bath. Similar results are found for both fibres and fabrics. The relation between set (S) and time of treatment (t) is found experimentally to be $S = k + a \log t$ where k and a are constants related to the pH and temperature of the setting bath respectively. There is a sharp increase in k at pH 9 (40°C.), pH 7-8 (70°C.) and pH 3-4 (100°C.). The values of a show maxima at pH 7 (100°C.) and pH 9 (70°C.) but only increase to pH 11 (40°C.) beyond which the experiments were not continued. There is no pH of the setting bath at which maximum set is obtained. Even in acid conditions the set is not constant, although pH 5 for the soaking bath gives maximum set, this being attributed to the blocking of amino groups by H^+ .

IV—Effect of Cooling on Setting

The effects of the temperature of the cooling water on the stress and other mechanical properties of the fibres and fabrics during the hot-water setting are studied. Where the specimens are dried under conditions of restraint, the temperature of the cooling water has no effect. If, however, the specimens are allowed to dry freely, a maximum set is obtained when the cooling water is at 20°C. The stress in single fibres stretched 5% rises suddenly on cooling after treatment in hot water, and is greatest when water is at 70°C. On grey fabric this maximum is at 55°C.; when hot water is at 75-80°C. the stress is reversed on cooling. These variations are attributed to a contractive force due to the entropy effect and the formation of cross-links on cooling.

L.P.

Setting of Wool Fibres. V—Application of Chemical Reagents

F. Bekku and N. Azuma

J. Soc. Textile Cellulose Ind. Japan., **15**, 133-137 (Feb 1959)

In attempt to re-form cross-links between polypeptide chains after reduction with thioglycolic acid, HCHO is also used. A high degree of set is obtained outside the isoelectric region by treatment with thioglycolic acid, although that in the alkaline region is attributed to the alkali itself. A definite concentration of thioglycolic acid, depending on the temperature (especially in the region 40-90°C.), gives rise to maximum set. Long periods of rinsing enhance the set; this is attributed to re-formation of cross-links and not necessarily to removal of thioglycolic acid. After-treatment with H_2O_2 also increases set,

although some fibre damage results. For this reason the view that the cystine link is re-formed by oxidation is not supported. Aqueous HCHO also promotes set, the degree being dependent on pH, concentration, and temperature of treatment. Since the alkali solubility of the fibre is reduced, formation of methylene cross-links may occur.

L.P.

Shrinkproofing of Woven Wool Fabrics

C.S.I.R.O. (Australia), Div. Textile Ind.,

Wool Research Lab. Report No. G8 (Aug 1959) pp. 3

Treatment with $KMnO_4$ in conc. brine followed by clearing with $NaHSO_3$ can readily be carried out in standard dyehouse equipment. No analyses are required of either the reagents or the liquors. The $KMnO_4$ treatment is complete when the solution becomes colourless and cleaning is complete as soon as the MnO_2 is removed from the wool. For economy, the brine should be used as a standing bath. The process is particularly suitable for blankets and for fabrics to be given a non-iron finish as described in Report No. G9 (see next abstract).

C.O.C.

Non-iron Effects in Shrinkproofed Woven Wool Fabrics

C.S.I.R.O. (Australia), Div. Textile Ind.,

Wool Research Lab. Report No. G9 (Aug 1959) pp. 6

Gives the necessary practical details and advice for the use of aq. $NaHSO_3$ to produce a non-iron finish. It should be applied as near as possible to the end of finishing and must not be done until all operations likely to give warp extension have been completed. Piece dyed cloths should be dyed after shrinkproofing and before setting, but cloths for printing should be both shrinkproofed and set beforehand. The dry cloth, brought to pH 5, is impregnated with a 1% solution of $NaHSO_3$ containing a wetting agent and without being dried, steamed in a blowing machine. Final drying must be carried out in absence of tension in both warp and weft in order to obtain a cloth free from residual relaxation shrinkage.

C.O.C.

Finishing of Fabrics containing Wool blended with Terylene or Acrylic Fibres

C. S. Whewell

J.S.D.C., **75**, 378-383 (July 1959)

Acrylonitrile-stabilised Wool Keratin Derivatives

Y. Tomimatsu, J. J. Bartulovich, and W. H. Ward

Text. Research J., **29**, 593-594 (July 1959)

Stenter Drying

T. A. Uthwatt and J. S. Woollatt

J.S.D.C., **75**, 445-451 (Sept 1959)

Changes of Colour caused by Fluorescent Brightening Agents

J. S. Ward and D. Blackburn

J.S.D.C., **75**, 493 (Oct 1959)

Influence of Various Additives on Soiling and Soil Removal Characteristics of Knitted Fabrics

AATCC Midwest Section

Amer. Dyestuff Rep., **47**, 933-940 (29 Dec 1958)

An account of co-operative work which shows (1) surface-active agents, particularly non-ionic, tend to decrease the dry soiling resistance of most fibres, (2) of the additives tested, colloidal silica finishes, developed for use as soil retardants, significantly improve the soil resistance of all fibres except Dacron, (3) the soil resistance of Dacron decreases when additives are present, (4) soil removal by washing generally remains unaffected by most additives.

C.O.C.

"I want to return it because"

G. M. Smith

Amer. Dyestuff Rep., **47**, 891-4 (15 Dec 1958)

Review by a large retailer of the complaints received from customers about wash-and-wear garments.

C.O.C.

PATENTS**Dimensional Stabilisation of Cellulosic Materials**

Upson Co.

USP 2,891,019

Cellulosic material is impregnated with an aqueous solution of an organic compound containing several hydroxyl groups at least one of which is part of a carboxyl group, in presence of sufficient ammonia of a volatile amine to bring the solution to pH ≤ 4 . Thus rayon gaberdine was impregnated with a 20% aqueous solution of diammonium sebacate so that after drying and baking it had an increase in weight of 21%. This reduced wet shrinkage by 8% and warp shrinkage by 60%. C.O.C.

Flame-resistant Finish Fast to Washing

U.S. Secretary of Agriculture

USP 2,891,877

Compounds containing \leq two 1-aziridinyl groups attached to pentavalent P atoms polymerise when heated in presence of trace quantities of water to yield products containing the recurring structure $\text{P-N-CH}_2\text{-CH}_2\text{-N-P}$ in which the P atoms are pentavalent. When formed *in situ* in hydrophilic fibrous organic material they reduce the combustibility and resist removal by washing and similar treatments. On hydrophobic materials they form flame-resistant coatings. Thus cotton cloth impregnated with 65% of its weight of an aqueous solution containing 25% tris(1-aziridinyl)phosphine oxide, 4% triethanolamine and 2% cationic softener at pH 9.4 and dried for 3 min. at 140°C. had excellent flame resistance even after being boiled for 3 hr. in a solution of soap and Na_2CO_3 . The handle of the cloth was unaffected by the treatment.

C.O.C.

Reducing the Felting Power of Wool by Treatment with Chromium Complexes

U.S. Secretary of Agriculture

USP 2,890,926

Treatment with a chromium complex of a carboxylic acid is used, the effect being increased if the wool is first rendered alkaline. Thus solvent-extracted wool cloth was treated first with aqueous sodium borate and then with an aqueous solution of the commercial chromium complex FC-804 (Minnesota Mining & Manufacturing Co.) whose production is described in USP 2,662,835 (J.S.D.C., 71, 108 (1955)).

C.O.C.

Chlorinating Wool to reduce its Felting and Creasing Properties

Gy

BP 822,735

When chlorinating wool in acid solution the process is slowed down with resulting more uniform treatment if a hydroxyalkylated-2,4,6-triamino-1,3,5-triazinyl compound having at the 3 amino N atoms \leq 4 H atoms but no aromatic substituents and at least 2 C atoms in each hydroxyalkyl group is present. Thus wool hanks (5 parts) are treated in water (150), 98% H_2SO_4 (0.3), and 2-mono-hydroxyethylamino-4,6-diamino-1,3,5-triazine at 15–20°C. A dilute hypochlorite solution containing active chlorine (0.075) is added to the bath during 15 min. After 30 min. NaHSO_3 is added to the bath as a dechlorinating agent. The finished yarn resists creasing and dyes very levelly.

C.O.C.

Cyanoethylation of Wool

American Cyanamid Co.

USP 2,890,925

Wool is treated with $>$ 5 times its volume of 0.001–0.4% aq. NaOH and then with at least half its weight of acrylonitrile at 50–80°C. The wool increases 1.5% in weight and 0.4% in N content and has very marked increase in affinity for acid dyes. Within wide limits the increased rate of exhaustion of an acid dyebath by cyanoethylated wool and the increased depth of the dyeing are roughly proportional to the degree of cyanoethylation.

C.O.C.

Modifying the Properties of Polyester Fibres and Foils

FH

BP 822,483

Treatment with a swelling agent either alone or in organic solvent solution at room temperature or above so that the swelling agent diffuses into the polyester much improves the affinity for dyes and also gives increase in moisture absorption and antistatic properties. Thus polyester fibre is impregnated at 60°C. with a methanol solution of formaldehyde diphenylacetal, dried or steamed for 15 min. at 130°C. It can then be dyed with disperse dyes without use of pressure equipment or carriers.

C.O.C.

Amylhydrosilicones as Water-repellent Finishing Agents

Monsanto Chemicals

BP 822,673

Treatment with an amyl hydrosilicone in presence of a Ti catalyst yields a water repellent finish with a very pleasant handle.

C.O.C.

Patterned or Textured Crêpe-like Effects

Heberlein & Co.

BP 822,597

Modification of BP 796,933 (J.S.D.C., 74, 673 (1958)). Use of a fabric having in warp and/or weft synthetic fibre yarns that have been made highly elastic by crimping results in patterned crêpe-like effects. Alternatively a fabric may be used which has been textured by mechanical deformation.

C.O.C.

Increasing the Soil-resistance of Fibres

DuP

USP 2,891,878

Treats with an aluminium formate and silica sol in which silica:alumina::3–30:1. The pH of the sol should be 3.0–5.5 and the silica particles have average diameter 3–150 m μ . The sol exhausts from an aqueous bath onto rayon and other textile fibres and is compatible with softeners and anionic surfactants. The treated fibres have a soft and pleasant handle.

C.O.C.

Sriferst Urea-formaldehyde Resins and Stabaca Catalysts in Textile Finishing (III p. 44)

Primers for Vinyl Chloride Resin Coatings (III p. 45)

Properties and Application of Urethane Coatings (V p. 53)

Chemical Modification of Flax Cellulose. I—Action of Acrylonitrile, Chloroacetic Acid, and β -Propiolactone (VI p. 53)

Effect of Temperature on the Felting and Dyeing Properties of Wool (VI p. 54)

Permanent Set, Supercontraction, Urea-bisulphite Solubility, The Proton Transfer Nature of Some Changes in Keratin and the Analogy with Muscle Contraction (VI p. 54)

Dimensional Changes of Textile Fibres on Calendering (VI p. 55)

Effect of Calcium Thiocyanate Solutions on Cellulose (XI p. 61)

Oxidative Degradation of Alkali Cellulose through Oxygen and Air (XI p. 61)

Formative of Graft Copolymers by the Ozonation of Cellulose (XI p. 61)

Resin Finishing of Cellulose and Suitable Testing Methods (XIV p. 63)

XI—PAPER AND OTHER CELLULOSIC PRODUCTS**Investigations on Dissolving Pulp. XVIII—Microscopic Studies on Swelling and Dissolution of Cellulose**

T. Koshizawa

J. Soc. Textile Cellulose Ind. Japan, 15, 95–102 (Feb 1959)

Microscopic investigation of the effect of H_3PO_4 treatment, xanthation, and acetylation on cellulose showed that the first two give similar swelling effects differing from that obtained by acetylation. This difference is ascribed to the higher rate of degradation and solubilisation of cellulose. Weak points in the outer layer of the fibre cause balloon-like swelling in H_3PO_4 or during xanthation, and cracks perpendicular to the fibre axis in acetylation. Photomicrographs of the fibre after various treatments are given.

L.P.

Action of Soda Solutions on Native Cellulose. Formation of Hydrated Sodium Cellulosate

G. Denoyelle

Svensk Papperstidning, 62, 390–406 (15 June 1959)

The linear relationship between the NaOH/cellulose ratio and the wt. of alkali cellulose/wt. of pulp ratio shows that alkali cellulose is composed of a stable cellulose-soda-water compound and of an impregnating soln. whose concn. at equilibrium is the same as that of the steeping soln.

The swelling of polyelectrolyte gels is not explained by Donnan's equilibrium theory which applies only to true solutions of non-diffusible electrolytes but is determined by a balance between cohesion and solvation energies taking account of the number of groups which have already reacted and the activity of the soln. This theory of swelling is applicable to intermolecular swelling as well as to that of fibres and of pulp sheets. 32 references. (In English.)

R.A.

Inductive Effects in the Hydrolysis of Cellulose Chains

B. G. Ranby and R. H. Marchessault

J. Polymer Sci., 36, 561–564 (April 1959)

The higher rate of hydrolysis of wood cellulose compared with that of cotton cellulose is due to the inductive effect on the acetal bonds of a small number of modified groups along the chains, e.g. carboxyl and carbonyl groups.

P.T.S.

The Part played by Molecular Interaction in the Hydrolysis of Polysaccharides in a Heterogeneous Medium

A. A. Konkin and Z. A. Rogovin

High Molecular Weight Compounds, 1, 177-181 (1959)
J. Polymer Sci., 38, 559 (Aug 1959)

A measure of the molecular interaction in hydrate cellulose, etc. was obtained from heats of swelling and water vapour sorption, and there was a direct correlation between these and the rate of hydrolysis. P.T.S.

Effect of Calcium Thiocyanate Solutions on Cellulose

O. Ant-Wuorinen and A. Visapää

Paperi ja Puu, 41, 344-349 (July 1959)

Accessibility of cellulose is identified with the accessibility of the carboxyl and carbonyl groups in it. 5 molar $\text{Ca}(\text{SCN})_2$ decreased accessible carboxyl and carbonyl content of cotton linters, bleached sulphite pulp and viscose rayon by 35-45%. The swelling effect of dilute thiocyanate is scarcely noticeable but becomes obvious at 2.0 M. and at 5.0 M. when a translucent gel forms becoming a fibrous mass on washing. $\text{Ca}(\text{SCN})_2$ affects X-ray characteristics. Native wood cellulose changes into cellulose II while native cotton cellulose is unaffected, confirming the opinion that crystallinity index (Cr. I) is a measure of average degree of order and density of packing of the crystalline portion of cellulose and not the percentual proportions of crystalline and amorphous material. (In English.) R.A.

Oxidative Degradation of Alkali Cellulose through Oxygen and Air

G. V. Schulz and F. Mertes

Das Papier, 13, 469-475 (Oct 1959)

Oxidative degradation is a four-stage process comprising: (1) splitting up of "weak bonds" with a half-value period of less than 15 min. (2) Pre-oxidation when β -glucosidic linkages are pre-oxidised without immediate decomposition in a very slow reaction, half-value period of about 13,000 hr. (3) Cleavage of pre-oxidised bonds by oxygen, half-value period 3.5 hr., consuming one mole O_2 . (4) After-oxidation, when approx. 2 glucose residues are decomposed using 3.5 moles of O_2 and producing 2 moles of CO_2 . It is unlikely that the intermediate stages can be characterised by molecular structural formulae. R.A.

X-Ray Study of Cellulose Complexes with Diamines Containing three, five, six, seven, and eight Carbon Atoms

J. J. Creely, L. Segal, and L. Loeb

J. Polymer Sci., 36, 205-214 (April 1959)

The distortion of the 101 interplanar spacing is related linearly to the number of carbon atoms in the diamine. The anhydroglucose-diamine ratio is approximately 2:1. Hydrazine and the seven and eight carbon diamines do not give satisfactory X-ray diagrams. P.T.S.

Nitrocarboxymethyl Cellulose

H. C. Haas and N. W. Schuler

J. Polymer Sci., 36, 447-452 (April 1959)

This derivative of cellulose shows good adhesion and is soluble in a variety of solvents including aqueous alkali. Preparation, infrared data, solubility, viscosity, and stability discussed. P.T.S.

Formation of Graft Copolymers by the Ozonation of Cellulose

V. A. Kargin, Kh. U. Usmanov, and B. I. Aikhodzhaev

High Molecular Weight Compounds, 1, 149-151 (1959)

J. Polymer Sci., 38, 287 (July 1959)

Active peroxide radicals on ozonated cellulose will initiate the polymerisation of styrene and a graft copolymer can be formed (6-6% styrene by weight). The grafting of styrene on to viscose cord increases its adhesion to rubber. P.T.S.

Synthesis of N-Substituted Amino Acid Esters of Cellulose

Lin'-Yan', V. A. Derevitskaya, and Z. A. Rogovin

High Molecular Weight Compounds, 1, 157-161 (1959)

J. Polymer Sci., 38, 288 (July 1959)

Light-scattering Measurements on Viscose Solutions

P. F. Onyon *J. Polymer Sci.*, 37, 295-304 (May 1959)

The effect of ageing on molecular weight and second virial coefficient have been investigated for two viscose solutions differing only in initial degree of xanthation. The presence of a small fraction of material of very high

molecular weight has been demonstrated. An exploratory study. P.T.S.

PATENTS

Improving Dry-strength of Paper

American Cyanamid

USP 2,884,057

A hydrophilic water-sol. cationic linear polyalkane polymer of mol.wt. 10,000-200,000 and containing 1-15 quaternary ammonium groups per 1000 linear chain atoms added to the pulp (0.01-5% on wt. of fibres) gives improved dry strength to paper made from the slurry. R.A.

Amphoteric Polymers for Improving Dry Strength of Paper

American Cyanamid

USP 2,884,058

Water-sol. linear amphoteric polymers in which the ratio of the total number of carboxylic, amide, and quaternary ammonium groups to the total number of linear carbon atoms forming the chain is $> 1:4$, are used as additives. As the polymers are cellulose-substantive no precipitant need be added, but the dry strength is improved even further when adsorption is assisted by the addition of alum. R.A.

Structure of Cellulose (VI p. 53)

Infrared Spectra of Crystalline Polysaccharides. I—

Hydrogen Bonds in Native Cellulose (VI p. 53)

X-Ray Study of Partially Benzoylated Cotton Cellulose (VI p. 53)

Sorption of Water Vapour by Cellulose and Polyvinyl Alcohol at High Humidities (VI p. 53)

Effect of Coagulation on Structure of Regenerated Cellulose. I—Studies on Model Cellulose Gels Coagulated from Viscose by Two-bath Treatments (VI p. 54)

The Photochemistry of Cellulose Acetate (VI p. 55)

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

The Relation between Configuration of Fibrous Proteins and their Chemical Structure (VI p. 54)

XIII—RUBBER; RESINS; PLASTICS

Synthesis of Starch and Styrene Graft Copolymers and a Study of their Properties

V. A. Kargin, P. V. Kozlov, N. A. Plate, and I. I. Konoreva

High Molecular Weight Compounds, 1, 114-122 (1959)

J. Polymer Sci., 38, 285 (July 1959)

Active peroxide groups are formed on starch in ozonated aqueous starch suspensions. These have been used to form graft copolymers between starch and polystyrene. P.T.S.

Formation of Polyamide Resins. IX—Alkaline Polymerisation of ϵ -Caprolactam

A. S. Shpital'nĭi and M. A. Shpital'nĭi

Zhur. obshch. khim., 29, 1285-1289 (April 1959)

Control of polymerisation of ϵ -caprolactam by metallic sodium has been investigated; occurrence of a lactam ring in an end group is indicated. G.J.K.

Measurement of Birefringence of Polyethylene Terephthalate Films

G. L. Berestneva and P. V. Kozlov

High Molecular Weight Compounds, 1, 126-127 (1959)

J. Polymer Sci., 38, 286 (July 1959)

Polyethylene Terephthalate Infrared Spectrum

A. Miyake

I—The Effect of Crystallisation

J. Polymer Sci., 38, 479-495 (Aug 1959)

Infrared changes in the infrared absorption spectra were followed as amorphous films of polyethylene terephthalate were drawn and heated. The main crystalline bands and all the amorphous bands are associated with the ethylene glycol residue. On crystallisation a *gauche* form of the ethylene glycol residue changes to a *trans* form.

II—Polyethylene- d_4 Terephthalate

Ibid., 497-512

The polymer was prepared using $\text{HOCD}_2\text{CD}_2\text{OH}$ and dimethyl terephthalate, and the infrared spectrum confirms the conclusions in Part I. P.T.S.

Photolysis of Polyethylene TerephthalateK. R. Osborn *J. Polymer Sci.*, **38**, 357-367 (Aug 1959)

The rate of bond rupture upon exposure to a carbon arc and a fluorescent sunlamp was measured by the change in molecular weight. The rate of energy absorption upon exposure to near ultraviolet light was determined from the absorption characteristics of the polymer and the emission characteristics of the light sources. The low quantum yield appears to be a result of the rapid recombination of free radicals immobilised in the solid state. P.T.S.

Extension of Crystalline and Vitreous Films of Polyethylene Terephthalate

P. V. Kozlov, V. A. Kabanov, and A. A. Frolova

High Molecular Weight Compounds, **1**, 324-329 (1959)*J. Polymer Sci.*, **38**, 566 (Aug 1959)

Necking is not due to phase transitions, but is of a relaxation nature. P.T.S.

Ultraviolet Absorbers for Plastics

R. A. Coleman and J. A. Weicksel

Modern Plastics, 195-198 (Aug 1959)

A survey of the literature, 25 references. C.O.C.

PATENT

Porous Flexible Synthetic Resin Sheet

T. J. Smith & Nephew

BP 822,051

Plastic sheeting under slight tension is treated with a comb of fine pointed stiff wires ("needles") arranged in a row. This comb is given a high rate of reciprocation of small amplitude so that they pierce the sheeting which is supported on a resilient backing. The sheeting is moved slightly each time the comb is withdrawn so that rows of pores are formed in the sheeting. This renders the sheeting sufficiently permeable to water vapour as to make it suitable for use as waterproof clothing. C.O.C.

Primers for Vinyl Chloride Resin Coatings (III p. 45)

Sorption of Water Vapour by Cellulose and Polyvinyl Alcohol at High Humidities (VI p. 53)

6,6-Nylon Molecular Weight Distribution (VI p. 55)

Re-equilibration of Poly- ω -aminocaproic Acid. Masking of Amino and Carboxyl Endgroups Due to a Reaction with an Isocyanic Acid Ester (VI p. 55)Rate of Formation of ϵ -Caprolactam upon Equilibration of Extracted Poly- ϵ -aminocaproic Acid Polymers (VI p. 55)

Electron Microscope and Electron Diffraction Investigations of the Crystalline Texture of Polyamides (VI p. 55)

Natural and Artificial Ageing of High Polymer Fibres (VI p. 55)

Strain-induced Crystallisation in Polyethylene Terephthalate (VI p. 55)

Acrylonitrile Polymerisation Kinetics (VI p. 55)

Modifying the Properties of Polyester Fibres and Foils (X p. 60)

XIV—ANALYSIS; TESTING; APPARATUS**Liquid Circulation Cell for Microscopical Use**

N. Iwanow and R. Schneider

Bull. Inst. Text. France, (78), 27-36 (Dec. 1958)

Details are given of a liquid circulation cell for the microscopical investigation of dyeing and other processes. J.C.F.

Microfiltration Apparatus

N. Iwanow and R. Schneider

Bull. Inst. Text. France, (78), 37-43 (Dec. 1958)

The suspension to be filtered (0.5-2 ml.) is contained in a short length of glass tubing which is pressed against the slide on to which the suspended material is to be deposited. The lower end of the tube is ground to a degree of roughness which depends on the dimensions of the particles in suspension. Compression of the air in the tube causes the liquid to flow out between the tube and the slide. Detailed instructions for the grinding process are given. J.C.F.

Fading of Dyes by Fluorescent LightH. Zukriegel *Melliand Textilber.*, **40**, 772-773 (July 1959)

Previous work on light fastness and extinction curves of dyes led to the relationships $L = 14 - \frac{10,800}{4000 \cdot \lambda}$, where L signifies light fastness rating and λ the wavelength in Å. corresponding to the first absorption maximum found on

the shorter wavelength side of 3229Å., and to the finding that dyes are destroyed by radiation of ≤ 3229 Å. and 4000-4771Å., but not by the intervening wavelength region. Energy distribution of six Philips fluorescent tubes are reproduced with colour temperatures of 3000°K. to 6,500°K. The proportion of energy in the 4,200-4600Å. region range from 0.38% ("Warmwhite de Luxe") to 1.10% ("Cool Daylight") of the total, so that this type of illumination causes little or no fading. S.M.J.

Optical Wrinklemeter

R. S. Hunter and C. A. Lofland

Amer. Dyestuff Rep., **48**, 54-58 (20 April 1959)

Apparatus to measure the degree of wrinkling of a fabric employs a parallel beam of light incident at 72° to the normal to the fabric specimen with two photoelectric cells to measure the scattered light set at 85° to the normal, one set below the light source and the other in the azimuth of the beam. The difference in response between the two photoelectric cells is measured and used to define the degree of wrinkling. Correlation between the instrument reading and visual assessment has been found with different samples of the same fabric in some cases but not in others. Samples of different fabrics cannot be compared. E.C.

Paper-chromatographic Resin AnalysisK. H. Pfaff *Melliand Textilber.*, **40**, 802-805 (July 1959)

Fabrics are successively extracted with hot CCl_4 , $\text{C}_2\text{H}_5\text{OH}$ and water, hydrolysed for 2 hr. with 1% HCl , and hydrolysates are separated by descending paper chromatography with 3:1:1 butanol-ethanol-water, together with a control hydrolysate from 1.5 g. urea, 0.5 g. ethylene urea and 0.2 g. melamine (which gives the strongest spot). For development one sprays with 1:1 30% HCHO -10% NH_4NO_3 (+ 1:1 30% HCHO -10% CH_3COONa for ethyleneurea), irons at 180°C. for 20-40 sec. and dyes for 2 min. at 60°C. with 0.2 g. Aeilancromotop RR and 0.2 g. 60% CH_3COOH per litre. Approximate R_f values are ethyleneurea 0.10, melamine 0.17, urea 0.33. Tetramethylolacetylenediurea and epoxy resins do not react usefully. S.M.J.

Rotproofing Textiles and Suitable Testing Methods

W. Hausam and R. Rupp

Melliand Textilber., **40**, 658-660 (June 1959)

The proposed German standard method for testing resistance to cellulose-destroying fungi involves deposition of the test sample on a 14 day old fungal culture on an agar-based nutrient. Experiments with *Chaetomium globosum* show, by means of reduction in wet breaking load, that this permits appreciable attack by cellulase-containing enzymes present in the nutrient, before fungi grow on the sample. This corroborates previous work with *Myrothecium verrucaria* (*Melliand Textilber.*, **39**, 429). The proposed method is therefore regarded as unrealistic, as preservatives should prevent the growth of fungi first and foremost. Comparison of alternative methods leads the authors to recommend, as most realistic, spraying spores on to the test sample lying on a nutrient. This corresponds with Swiss and American standard methods. Alternatively, the proposed German method can with advantage be adapted by interposing wire mesh between culture and test sample. Fungal growth is then unhindered, whereas direct contact of the sample with previously formed enzyme is largely precluded. S.M.J.

Development of a Comparative Method for Evaluation of the Mothproofness of Wool Serge

H. J. Hueck

Ann. Appl. Biol., **46**, 511-528 (1958)*Chem. Abs.*, **53**, 15457 (25 Aug. 1959)

Existing test methods have been compared in inter-laboratory experiments and found to be wanting in accuracy and agreement. Accuracy was much increased by comparing loss in weight caused by larvae of *Tineola biselliella*, *Attagenus piceus* or *Anthrenus vorax* to a test sample with that of a standard wool serge treated with a standard mothproofing agent, e.g. dinitro- α -naphthol. A tolerance level of 0.8% was set for mothproofness of wool serge. C.O.C.

Applications of Infrared Spectroscopy to Cellulose Chemistry

F. Hurtubise

Canadian Textile J., **76**, 53-60 (12 June 1959)

The nature of infrared radiation, its interaction with molecules and the technique of infrared studies of fibres

are outlined. Applications of infrared spectroscopy to studies of the structure, degradation, and configuration of cellulose are briefly reviewed and examples of its use in quantitative and qualitative analysis are given.

W.R.M.

Design of a Method for Testing the Fastness of Coloured Leathers to Dry Cleaning

E. J. Davies and H. E. Nursten

J. Soc. Leather Trades Chem., **43**, 319–327 (Sept. 1959)
A report of the work carried out with respect to organic solvents by the S.L.T.C. Fastness Tests Committee, leading to the Provisional Method (*ibid.*, **42**, 74, 1958). The present practice of dry-cleaning leather is outlined.

J.W.D.

Mould-proofing of Leather—Comparison of Methods for Evaluating Mould Resistance

G. H. Green

J. Soc. Leather Trades Chem., **43**, 212–220 (June 1959)
Published methods of comparing fungicidal activities and methods of assessing the effectiveness of mould-proofing treatments are reviewed with particular reference to conditions of incubation; inoculation of the leather; incubation period; volatility, stability, and solubility in water, of the fungicide; and method of sampling. Three test methods, differing in the method of inoculating the samples, have been applied using four fungicides; both methods and fungicides are compared. A new test method is described which is believed to be more stringent than hitherto-published methods, taking into account the volatility and stability of the fungicide. In the case of phenolic fungicides a rough comparison of volatility may be made.

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J.W.D.

Estimation of Double Bonds in Acrylic Esters

U. Bartels and H. Hoyme

Faserforsch. und Textiltech., **10**, 345–347 (July 1959)
A complexometric titration method is described and results compared with those obtained using the mercuric acetate and pyridine sulphate dibromide methods.

W.R.M.

About pH

D. A. Clibbens *J. Textile Inst.*, **50**, p 522–542 (Sept 1959)
An explanation for textile technologists of pH in which it is stated that no useful purpose can be served by attempting to give short, nominally simple explanations of pH. Instead pH is presented as being primarily an arbitrary scale for measuring acidity and alkalinity.

C.O.C.

Polydispersed Analysis of Vat Dyes using Test-tube Centrifuge

R. V. Voitsekhovskii and T. K. Zasluchuk

Ukrain. khim. zhur., **25**, 239–244 (May 1959)
A method of separating vat pigment dispersions into six fractions (2.0–0.125 μ) by a laboratory centrifugal technique is used to show the variation of the fraction composition in different dyes. The mathematical treatment of T. Svedberg (*Koll. Zeitschr. Erg. Bd.*, **36**, 53 (1925)) for particle size is applied.

G.J.K.

Interaction of Surface Films with Solute in Solution

M. Muramatsu

I—Potentiometric Titration of Aqueous Dye Solution and Calculation of the Ionisation Constant of the Dye

Bull. Chem. Soc. Japan, **31**, 864–871 (Oct 1958)

II—Sorption of Dye on a Built-up Film of Stearic Acid and Barium Stearate

Ibid., 871–877

III—Effect of Dissolved Dyes upon a Monolayer of Octadecylamine

Ibid., 878–882

Determination of Chlorine in Wood Pulp and Paper

P. O. Bethge and T. Tröng

Svensk Papperstidning, **62**, 598–601 (15 Sept 1959)
Conventional ashing methods are not satisfactory for trace amounts of chlorine but combustion in oxygen in a closed vessel, followed by potentiometric titration with AgNO_3 in acid soln., is suitable for chlorine content $> 0.1 \text{ mg./g.}$ Combustion of the sample (500–700 mg.), attached to a tungsten spiral, was carried out in a flask flooded with oxygen and containing some 10 ml. de-ionised water to absorb CO_2 . With very low chlorine content up to ten combustions were carried out using the same absorption soln. The chloride in the soln. was determined potentiometrically, using a Radiometer PHM3 valve

potentiometer, with a Ag-AgCl electrode and a calomel electrode connected to the soln. by a 10% ammonium nitrate soln. liquid bridge. The Schöniger flask used in the combustion is described in *Mikrochim. Acta*, (1955) 123. For smooth combustion wood was ground finely and pressed into tablets and paper was rolled tightly. (*In English.*)

R.A.

Determination of Methoxyl

H. Sobue

J. Soc. Textile Cellulose Ind. Japan, **15**, 21–23 (Jan 1959)

A modification of Zeisel's method, suitable for sulphur-containing compounds. The sample is heated with HI, and the CH_3I formed, carried from the reaction by a current of CO_2 from which it is absorbed into pyridine. Methyl pyridinium iodide ($\lambda_{\text{max}} = 366 \text{ m}\mu$; $\epsilon = 620$) is formed and since its solutions obey Beer's law, the methoxyl value of samples can be rapidly and accurately measured.

L.P.

Polarographic Examination of Vat Dyeing Solutions

F. Péter *Magyar Textiltechnika*, **10**, (4–5), 154–157 (1958)
Hungarian Tech. Abs., **11**, (1), 18 (1959)

In basic solutions containing dithionite and leuco vat dyes the polarogram of dithionite is distorted by presence of the leuco compound above a certain critical concentration. This critical concentration, which depends upon the nature of the dye, can be determined by oxidising the leuco dye in alkaline medium and filtering, drying, and weighing the precipitate produced. The amount of the leuco dye can be brought below the critical concentration by dilution, thus the concentration of dithionite can be determined. The same end may be achieved also by measuring the cathodic wave of dithionite which may readily be determined above 20°C . The polarographic activity of leuco vat dyes permits determination of the dye concentration. Interference by dithionite is eliminated by cooling or by thermal decomposition. The polarographic method developed for analysis of vat dye solutions affords a possibility of studying the reduction and oxidation processes of vat dyes by the determination of reaction rates and equilibrium data.

C.O.C.

Analysis of Finish in Textiles—A.A.T.C.C. Tentative Test Method 94–1959

AATCC Committee on Identification of Finishes on Textiles *Amer. Dyestuff Rep.*, **48**, 129–133 (21 Sept 1959)

Colorimetric Determination of Urea in Urea-formaldehyde Resins

M. L. Adams and M. H. Swann

Off. Dig. Fed. Paint Yarn. Prod. Cl., **31**, 1247–1251 (Oct 1959)

The urea content of urea-formaldehyde resin solutions singly or mixed with melamine resins can be measured by the yellow developed with *p*-dimethylaminobenzaldehyde. The resins are first hydrolysed in methyl alcohol with hydrochloric acid. Full working details are given.

C.O.C.

Resin Finishing of Cellulose and Suitable Testing Methods

K. May, O. Rothe, and L. May

Melliand Textilber., **40**, 899–905 (Aug 1959)

After reviewing differences between cotton and wool, methods available for improving crease resistance of the former, and chemical analysis of finishes, paper-chromatographic and electrophoretic analyses of resin precondensates and hydrolysates are discussed and illustrated in detail. The authors prefer ascending chromatograms in 3:1:1 butanol-ethanol-water or 4:1 propanol-water, and tabulate R_f values under specific conditions, ranging from the least mobile methylolmelamine and methylol-urea precondensates to the most mobile corresponding etherified derivatives. For development Neocarmin W or Crystal Ponceau 6R (C.I. Acid Red 44) are suggested, alternatively colour reactions with ferricyanide and nitroprusside. In electrophoresis melamine moves towards the negative, urea towards the positive pole.

S.M.J.

Determining Presence of Mercerisation in Cotton—A.A.T.C.C. Tentative Test Method 89–1958

S. M. Edelstein

Amer. Dyestuff Rep., **47**, 941–942 (29 Dec 1958)

An account of the work of A.A.T.C.C.'s A committee which led to acceptance of the above test.

C.O.C.

Work of A.A.T.C.C. Committee on Colorfastness to Light

J. E. Norton

Amer. Dyestuff Rep., **48**, 12-13 (12 Jan 1959)

Report of the Chairman on the year's work. C.O.C.

Work of A.A.T.C.C. Committee on Colorfastness to Washing

R. B. Smith

Amer. Dyestuff Rep., **48**, 18-20 (12 Jan 1959)

Chairman's report on the year's work. C.O.C.

Colorfastness to Bleaching—A.A.T.C.C. Tentative Test Method 31-1958*Amer. Dyestuff Rep.*, **47**, 443 (29 Dec 1958)

Report of A.A.T.C.C. Committee on Colorfastness to Bleaching.

Work of A.A.T.C.C. Committee on Damage caused by Retained Chlorine

R. F. Aurich

Amer. Dyestuff Rep., **48**, 14-16 (12 Jan 1959)

Report of the Chairman on the year's work. C.O.C.

Damage caused by Retained Chlorine—A.A.T.C.C. Tentative Test Method 92-1958A.A.T.C.C. Committee on Damage caused by Retained Chlorine *Amer. Dyestuff Rep.*, **48**, 5-7 (12 Jan 1959)**Work of the A.A.T.C.C. Committee on Dimensional Changes in Textile Fibres**

E. Artim

Amer. Dyestuff Rep., **48**, 21-22 (12 Jan 1959)

Secretary's report on the year's work. C.O.C.

Dimensional Restorability of Woven Textiles after Laundering—A.A.T.C.C. Tentative Test Method 95-1959AATCC Committee on Dimensional Changes in Textile Fabrics *Amer. Dyestuff Rep.*, **48**, 133-134 (21 Sept 1959)**Wash-and-Wear or Easy-care Testing Methods and Standards**

J. G. Stass

Amer. Dyestuff Rep., **47**, 888-890 (15 Dec 1958)

Review of current American practice. C.O.C.

Work of the A.A.T.C.C. Committee on Wash and Wear

G. M. Richardson

Amer. Dyestuff Rep., **48**, 20-21 (12 Jan 1959)

Report on the year's work. C.O.C.

Measurement of Resistance of Wool Textiles to Attack by Insect Pests

C. H. Bayley

Canadian Textile J., **76**, 49-51 (21 Aug 1959)

An introductory note giving details of the method for carrying out the test using the black carpet beetle, the method of determining damage and reporting are given. Procedure for rearing the beetles is given. The test is designated Method 38 (31 March 1958), Schedule 4-GP-2, Methods of Testing Textiles of the Canadian Government Specifications Board. P.G.M.

Abrasion Resistance of Fabrics—Evaluation of Wear by Means of the Accelerator—A.A.T.C.C. Tentative Test Method 93-1959

AATCC Committee on Resistance to Abrasion

Amer. Dyestuff Rep., **48**, 127-8 (21 Sept 1959)**Detection of Antibacterial Property of Fabrics—Agar Plate Method A.A.T.C.C. Tentative Test Method 90-1958**

AATCC Committee on Antibacterial Agents

Amer. Dyestuff Rep., **48**, 8-9 (12 Jan 1959)**Cotton Duck for Weathering Tests**

P. J. Hannan and S. Shapiro

J.S.D.C., **75**, 460 (Sept 1959)**Work of the A.A.T.C.C. Committee on Drycleaning Test Methods**

A. E. Johnson

Amer. Dyestuff Rep., **48**, 17-18 (12 Jan 1959)

Chairman's report on the year's work. C.O.C.

Procion Dye Staining for Differentiation of Skin and Core of Viscose Rayon Fibres

K. Kato

Text. Research J., **29**, 661-664 (Aug 1959)

Slide preparations of mounted fibre cross-sections were stained with an alkaline soln. of Procion Black HGS (ICI) to give a staining entirely selective for the skin area. Since the Procion dye reacted chemically with cellulose

molecules, it was probable that the differential staining produced by this technique was due to a definite difference existing between the skin and the core with respect to chemical reactivity towards the dye. This differentiation mechanism appeared quite different from that generally accepted to be the case in techniques using ordinary dyes. The results for several types of cellulose rayons showing various staining behaviours were in good agreement with those obtained by other stain methods. Application of the procedure to other fibres was found to give positive staining only to wool, silk, regenerated protein, and Vinyon fibres. Several typical photomicrographs are presented. S.B.D.

Estimation of the Parameters in the Mark-Houwink EquationJ. F. Voels *J. Polymer Sci.*, **36**, 333-339 (April 1959)

The Mark-Houwink equation connecting intrinsic viscosity and molecular weight of polymers involves two parameters which are usually determined empirically from many experimental values of the two quantities. This theoretical paper shows how a single determination can give the parameters, and shows that the method works in practice. P.T.S.

Fractionation of Polymers by Liquid-Liquid Distribution. I—On the Selection of Liquid Systems

K. E. Almin

Svensk Papperstidning, **62**, 594-597 (15 Sept 1959)

Liquid-liquid counter-current distribution is of limited application as it requires two immiscible solvents for the polymer. It is doubtful whether a two-phase liquid system composed of two pure components will fulfil the conditions. After discussing three component systems it is concluded that at least four components are required—utilising the miscibility of a solvent with liquids mutually immiscible. Experiments were made with *sec.*-cellulose acetates at room temp. in a solvent system of dimethyl sulphoxide, trichloroethylene, benzene, and water, giving two clear phases and a clear viscous phase containing the high molecular fraction. Counter-current distribution, according to Craig, in the same solvent system, can be applied to the cellulose acetate in the low viscosity phases. It is indicated that mol.wt. and not degree of substitution is the chief factor. The method is rapid (3 days) and no accurate temp. control is necessary. (*In English.*) R.A.

Optical Studies**I—Relation of Colour to the Apparent Soilability of Textile Materials**

H. B. Mann and T. H. Morton

J.S.D.C., **75**, 522-533 (Nov 1959)**II—SMR Values for a Comprehensive Range of Colours**

H. B. Mann

Ibid., 534-536**Breaking Load and Extension of Strips of Woven Fabric**

BS 2576:1959

This revised standard makes provision for strength tests by constant-rate-of-loading, constant-rate-of-traverse, and pendulum-type machines. C.O.C.

Separation, Estimation, Orientation, and Ultraviolet Spectra of Isomeric Azo Compounds formed by Diazo Coupling to 1-Naphthylamine and its Derivatives (IV p. 46)

Dimensional Changes of Textile Fibres on Calendering (VI p. 55)

XV— MISCELLANEOUS**PATENT****Coloured Anodised Aluminium**

Kaiser Aluminum and Chemical Corpn.

BP 820,583

An aluminium base alloy containing 0.2-0.5% of Cr and > 0.35% of Fe and Si is coloured bronze or gold by anodising it in an acid electrolyte at 60°F. for < 15 min. while maintaining an anode current density of < 5 amp. per sq.ft. The coating has excellent fastness to light. The exact colour obtained between bronze and gold is controlled by the addition of small amounts of other metals, e.g. Ti, Mg, Mn and Cu. C.O.C.

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